Journal of Catalysis 257 (2008) 255–261

Contents lists available at ScienceDirect

Journal of Catalysis

www.elsevier.com/locate/jcat

# Development of a transient response technique for heterogeneous catalysis in liquid phase, Part 2: Applying membrane inlet mass spectrometry (MIMS) for detection of dissolved gasses

D. Radivojević [a,b], M. Ruitenbeek [b], K. Seshan [a], L. Lefferts [a,*]

[a] *Catalytic Processes and Materials, Faculty of Science and Technology, Institute of Mechanics, Processes and Control Twente (IMPACT) and MESA+, University of Twente, P.O. Box 217, 7500AE Enschede, The Netherlands*
[b] *SABIC Europe R&D, P.O. Box 319, 6160 AH, Geleen, The Netherlands*

ARTICLE INFO

*Article history:*
Received 12 February 2008
Revised 29 April 2008
Accepted 1 May 2008
Available online 13 June 2008

*Keywords:*
Platinum dispersion
Liquid phase
Transient operated reactor
Dissolved gasses

ABSTRACT

A home-made analyzer for dissolved gasses in water, based on membrane inlet mass spectrometry (MIMS), was successfully applied for the first time as an in-line method for detection of gases dissolved in an aqueous stream, at the exit of a catalytic reactor in a transient experiment. The technique was applied for measuring the metal dispersion of three different catalysts (EuroPt-1, $Pt/SiO_2$ and Pt/CNF) in liquid phase via $H_2$–$O_2$ titration. The titration stoicheometry obtained (i.e. ratio of $H_2$ and $O_2$ consumption) is in agreement with the stoicheometry obtained in gas phase titration experiments in literature. The platinum dispersions obtained in liquid phase are in excellent agreement with dispersions based on hydrogen chemisorption in gas phase for all three catalysts. Clearly, water does not influence the accessibility of the Pt atoms, disagreeing with recent suggestions in literature. In addition, the detector is universal and allows calibration of $H_2$, $O_2$, $N_2$ and Ar dissolved in water with insignificant cross contamination. Despite the relatively slow dynamic response of the detector (between 4 min for hydrogen up to more than 40 min for oxygen), it was proven possible to perform quantitative experiments in pulse mode, with a detection limit in the order of 0.5 $m^2$ Pt. The capability of this method is further demonstrated by the surprising observation that dissolved hydrogen physisorbs significantly on a reduced Pt catalyst whereas dissolved oxygen does not interact with an oxidized catalyst.

## 1. Introduction

In part 1 of this paper [1], we reported on the development of a transient reactor with simultaneous analysis of the effluent using in-line ESI-MS (electrospray ionization mass spectrometry). With this technique it is possible to follow semi-quantitatively species formed during transient catalytic oxidation of glucose and catalytic reduction of nitrite in aqueous phase. Unfortunately, the limitation of this technique is the inability to detect gases dissolved in water, due to the relatively mild ionization process via electrospray. We therefore searched for alternative detectors for dissolved gasses.

Commercially available analyzers like Orbisphere [2] and Fugatron HYD 400 [3] are usually applied to analyze gases dissolved in liquids. Detection based on electrochemical reactions (Orbisphere analyzer) is usually lacking long term stability of the sensor. The Fugatron HYD 400 analyzer uses a coated probe permeable for dissolved gases, which improves the reliability of detection. These analyzers are able to detect single gasses present in liquids in industrial applications such as beverage production and nuclear power plants.

Home made analyzers such as Differential Electrochemical Mass Spectormetry (DEMS) [4,5] or Membrane Inlet Mass Spectrometry (MIMS) [6,24,25] are usually described for scientific applications. The principle of operation of DEMS and MIMS is similar, i.e. removal of gases from the solution via permeation through a hydrophobic membrane, such as a porous Teflon membrane in the case of DEMS and a dense polymeric rubber membrane in the case of MIMS. The permeated gas is analyzed with a mass spectrometer in both cases. For example, Kana et al. [6] used a technique based on the MIMS principle for determination of nitrogen and oxygen dissolved in sea water. Kostiainen et al. [7] used a concept similar to MIMS to analyze volatile organic compounds like toluene, *o*-xylene, MTBE and phenol in water. In order to test the suitability of such an analyzer for transient experiments, we have chosen $H_2$–$O_2$ titration experiments on supported platinum catalysts in water as a case study.

Supported platinum catalysts have been used in this study in view of its wide application [8] and Pt on carbon has been included because of its frequent application in liquid phase oxidation and hydrogenation reactions [9,10]. EuroPt-1 reference catalyst

---

[*] Corresponding author. Fax: +31 53 489 4683.
*E-mail address:* l.lefferts@tnw.utwente.nl (L. Lefferts).

0021-9517/$ – see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2008.05.011

(platinum supported on silica) was used because it is well characterized in many labs [11,12].

Hydrogen chemisorption is the standard technique to determine the dispersion of supported platinum catalysts [13,14]. This technique is however not directly applicable in liquid phase because desorption of chemisorbed hydrogen by heating is an essential step, which cannot be done in liquid phase. Hydrogen titration of pre-adsorbed oxygen on platinum is an even more sensitive method and especially suitable for the catalysts with a low metal loading. It was applied for the first time by Benson et al. [15] who observed a titration stoicheometry of $H_2$-chemisorption:$O_2$-chemisorption:$H_2$-titration = 1:1:3. This implies that hydrogen is consumed by both reaction with chemisorbed oxygen as well as by chemisorption on the metal. Consequently, if one assumes a Pt:O = 1:1 ratio, three atoms of hydrogen are consumed for every exposed platinum atom.

There are only two studies, to the best of our knowledge, addressing the question whether the presence of a liquid would influence the dispersion of supported precious-metal catalysts. Another issue is the question whether solvents would affect the dispersion measurement via influencing the chemisorption stoicheometry of oxygen and hydrogen. $CS_2$ was recently used as a probe molecule to determine Pd dispersion at the solid–liquid interface with transient pulse experiments [16]. It was claimed that the Pd dispersion obtained was approximately three times less than the dispersion obtained using gas phase ($H_2$ and CO) chemisorption (i.e. $D_L = 11\%$ vs $D_G = 36\%$). Bradley et al. [17] determined platinum dispersions with hydrogen chemisorption and compared the results with $H_2$–$O_2$ titrations, both in the liquid phase using a volumetric method. They found good agreement for dispersion measurements of colloidal polymer-supported platinum nanoclusters. Unfortunately, it is not clear how in this work an uncovered surface was obtained, which is necessary for the chemisorption experiment.

The volumetric method, as applied by Bradley et al. [17], is very sensitive for temperature deviations. The pulse flow technique, which has been successfully applied for dispersion determination of supported platinum in the gas phase, does not suffer from that problem. In principle, the same approach can be applied using gases dissolved in a liquid phase. However, the key challenge is to find a sensitive detector which allows on-line analysis of all dissolved gases present in the liquid phase.

We here report on the development and application of a detector similar to MIMS to perform $H_2$–$O_2$ titrations over a series of platinum catalysts (EuroPt-1, $Pt/SiO_2$ and Pt/CNF) in water. When successful, this detector can be coupled to the ESI-MS detection system in order to arrive at an universal transient technique for liquid phase experiments allowing detection of both organic compounds and ions (ESI-MS) as well as dissolved gases. To the best of our knowledge, application of pulse experiments with gases dissolved in water to determine platinum dispersions was not described before and we are reporting here on the influence of water on the interaction of hydrogen and oxygen with Pt.

## 2. Experimental

### 2.1. Materials

EuroPt-1 catalyst (6.3 ± 0.05 wt% Pt), obtained from Johnson–Matthey, was crushed and sieved and the fraction of 30–50 µm was used. $Pt/SiO_2$ and Pt/CNF supported on Ni-foam catalysts, as well as chemicals and gasses used, are described in detail in part 1 of this paper [1].

### 2.2. Methods

The Pt loading of the catalysts was determined with X-ray fluorescence spectroscopy (Phillips PW 1480 spectrometer). Platinum dispersions of EuroPt-1, $Pt/SiO_2$ and Pt/CNF catalysts were measured with hydrogen chemisorption (ChemiSorb 2750, Micromeritics). Platinum metal dispersion was calculated assuming H:$Pt_s$ ratio equal to one [18]. Metal particle sizes in fresh $Pt/SiO_2$ and Pt/CNF catalyst were also estimated with transmission electron microscopy (TEM) by averaging sizes of typically 100 platinum particles, using a Philips CM 30 microscope (300 kV).

#### 2.2.1. Experimental set-up

The experimental set-up was described in the first part, except for the detector.

*2.2.1.1. Analyzer for gases dissolved in liquid* The analyzer consisted of a probe (Fig. 1a) and the MS detector (Fig. 1b). The probe was made of perforated stainless steel tubing (1/16″, 40 holes with ∅ 0.25 mm, Fig. 1a) and covered with silicon rubber (1.0 × 1.4 mm, Vitton). Then, the probe was inserted into a Swagelock T joint adjusted to minimize dead volume (Fig. 1a). Gases can permeate from the liquid phase through silicon rubber to vacuum.

The permeating gas enters the low-vacuum part of the equipment (Fig. 1b) that typically operates at $5 \times 10^{-4}$ mbar. The permeating gas is then allowed to flow into the high vacuum part via a 1 µm orifice ($O_1$). Gases were analyzed in the MS chamber with a quadrupole mass spectrometer detector (QMG422, Pfeiffer Vacuum, with secondary electron multiplier), operated in “selected ion mode” and using electron impact ionization. The MS chamber is connected to a turbo-molecular pump (TSH 521, Pfeifer Vacuum) capable of creating vacuum in the range of $10^{-8}$ mbar. Valve $V_1$ closes automatically in case the pressure in the MS chamber exceeds a value of $10^{-5}$ mbar, in order to protect the mass spectrometer.

*2.2.1.2. Response time of detector* The response time of detector was determined by-passing the reactor with pulses of water (10 ml during 20 min with flow rate of 0.5 $\text{ml}\,\text{min}^{-1}$, Figs. 2a–2c) saturated with various gases (argon, hydrogen or oxygen). The response time was defined as the time required for the signal to reach a level of 95% of the final (stable) value. A delay of about 0.7 min was observed with all gases. The detector responds relatively fast to hydrogen (4 min, Fig. 2b) and somewhat slower to argon (8 min, Fig. 2a). The response to oxygen fails to stabilize within 40 min (Fig. 2c).

*2.2.1.3. Hydrodynamic behavior of reactors with different catalyst* The hydrodynamic behavior of the reactors loaded with the different catalyst supports (HPLC silica as well as CNFs without Pt) was checked with pulses saturated with inert Ar (10 ml during 20 min with flow rate 0.5 $\text{ml}\,\text{min}^{-1}$). Similar experiments with the by-pass and the empty reactor were performed for comparison.

*2.2.1.4. Calibration of gas analyzer in pulse-mode* The calibration of the detector was done with pulses (2.5 ml, during 5 min at flow rate 0.5 $\text{ml}\,\text{min}^{-1}$) of dissolved gases ($H_2$, $O_2$, Ar and $N_2$) in the absence of catalyst (blanks). The amount of the gases present in the pulses was varied by changing the partial pressure of gases in the saturator (partial pressure was adjusted with argon as a second gas) and the resulting concentrations of dissolved gases were calculated using Henry’s constants [19]. Calibration curves were obtained using the surface areas of pulses observed as a response from analyzer for species $m/z$ 2 (hydrogen), $m/z$ 28 (nitrogen), $m/z$ 32 (oxygen) and $m/z$ 40 (argon).

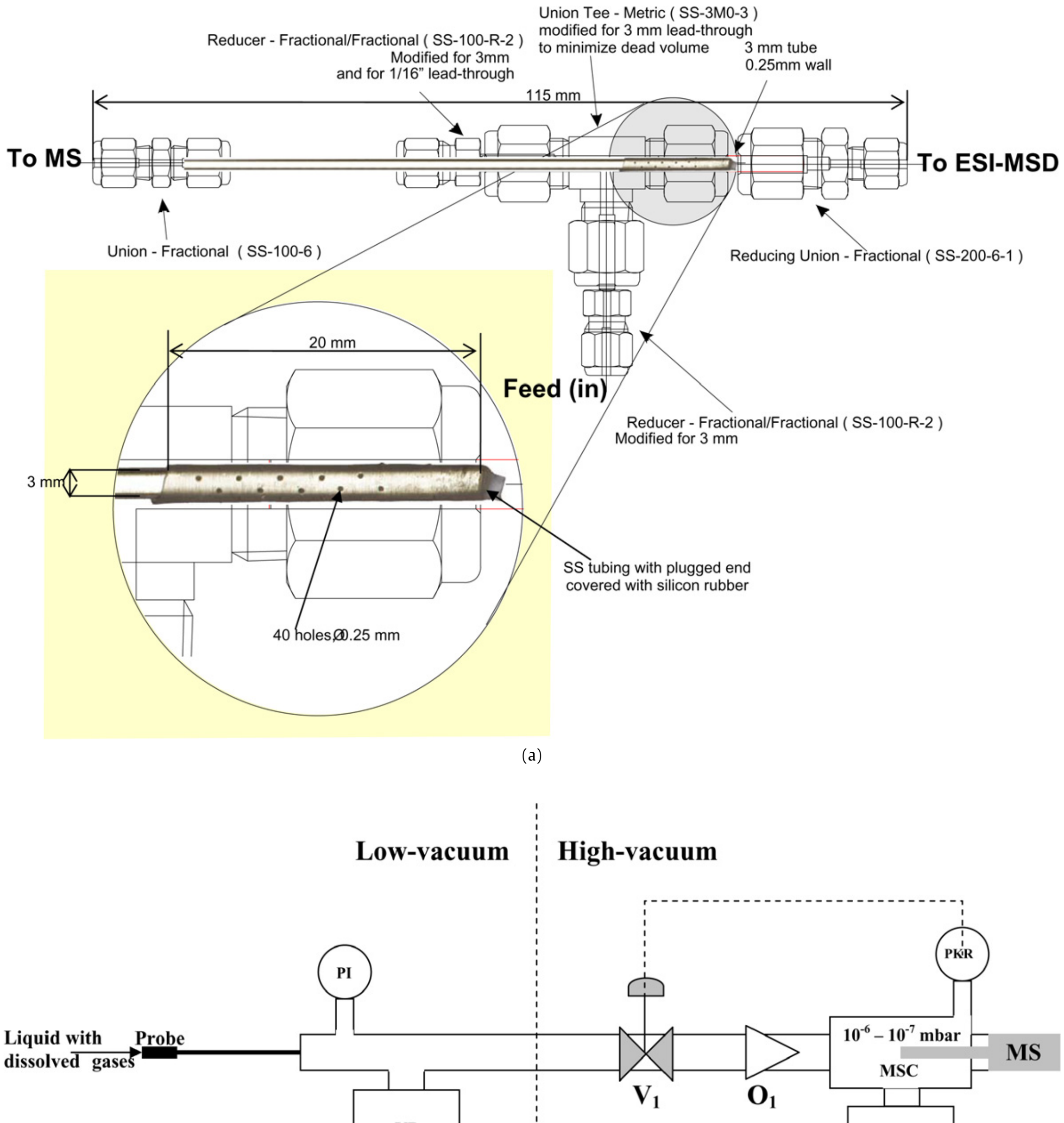
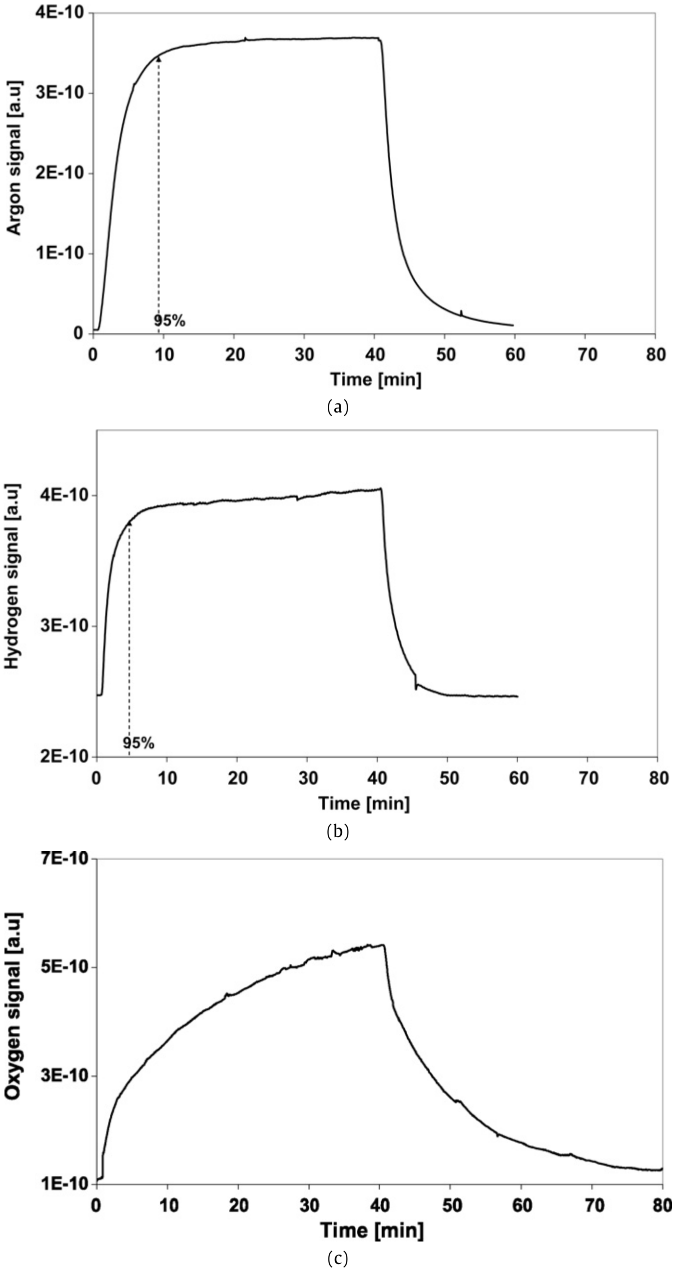


**Fig. 1.** (a) Schematic representation of the probe. (b) Schematic representation of the set-up based on MIMS principle for determination of gases dissolved in liquids. PI—pressure indicator, VP—vacuum pump, $V_1$—closing valve, $O_1$—orifice, PKR—pressure controller and regulator, MSC—mass spectrometer chamber, MS—mass spectrometer, TMP—turbo-molecular pump.

### 2.2.2. $H_2$–$O_2$ and $O_2$–$H_2$ titration experiments in liquid phase

Water in vessels 1 and 2 (see Fig. 1 in part 1 for details) was saturated with oxygen and hydrogen, respectively (30 min, 200 ml min$^{-1}$). Water in vessel 3 was flushed with argon (30 min, 200 ml min$^{-1}$), in order to remove any dissolved oxygen. Then, water saturated with oxygen (from vessel 1) was flown through the reactor during 30 min in order to pre-adsorb oxygen on the catalyst. Subsequently, pure water (from vessel 3) was flown through reactor during 30 min in order to remove any physisorbed oxygen from the catalyst and dissolved oxygen from the water present in the reactor. All experiments were performed with a flow rate of 0.5 ml min$^{-1}$.

Next, the oxygen-covered catalyst was contacted with pulses of hydrogen solution from vessel 2 (concentration $7.8 \times 10^{-4}$ mol/l, 2.5 ml during 5 min); pulses were repeated every 20 min, flowing water saturated with Ar between pulses. Also after the final pulse with hydrogen in water, Ar saturated water (from vessel 3) was flown through the reactor for 30 min, before pre-adsorbed hydrogen was titrated with pulses of oxygen solution (concentration $1.3 \times 10^{-3}$ mol/l, 2.5 ml during 5 min); again, pulses were re-



(a)

(b)

(c)

**Fig. 2.** (a) Response of the analyzer to a pulse of argon (20 ml, 40 min, $F = 0.5$ ml/min, $c_M(\mathrm{Ar}) = 1.4$ mM, $T = 295$ K). (b) Response of the analyzer to a pulse of hydrogen (20 mL, 40 min, $F = 0.5$ ml/min, $c_M(H_2) = 0.78$ mM, $T = 295$ K). (c) Response of the analyzer to a pulse of oxygen (20 mL, 40 min, $F = 0.5$ ml/min, $c_M(O_2) = 1.3$ mM, $T = 295$ K).

peated every 20 min. These sequences were subsequently repeated 3 times.

## 3. Results and discussion

First, the results of catalyst characterization will be presented and the hydrodynamic behavior of the reactors will be shortly discussed. Most importantly, results of $H_2$–$O_2$ titration experiments as well as the interaction between dissolved hydrogen and oxygen with the catalyst will be discussed.

### 3.1. *Catalyst preparation and characterization*

The platinum loading of the three catalysts was determined with XRF (Table 1). The platinum loading of the EuroPt-1 (6.3 ± 0.05 wt%) agrees well with literature data [11,12]. The platinum loadings of fresh Pt/SiO$_2$ and Pt/CNF (3 wt%) have been reported in part 1.

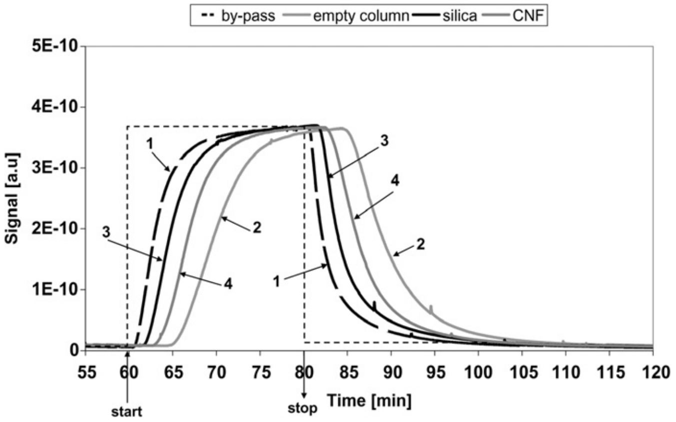


**Fig. 3.** Response of (1) by-pass, (2) empty column, (3) column with silica and (4) column with CNF to a pulse of argon (10 ml during 20 min with flow rate 0.5 ml min$^{-1}$, $c_M(\mathrm{Ar}) = 1.4$ mM, $T = 295$ K).

Table 1 also gives platinum dispersions measured with gas phase hydrogen chemisorption, resulting in 65% for EuroPt-1 and 61% for Pt/SiO$_2$. The Pt dispersion of Pt/CNF was 25%, as reported in detail in part 1 (see Table 2 in part 1).

### 3.2. *Response time of the detector*

The delay time observed in Figs. 2a–2c was 0.7 min, independent of the gas dissolved, well in agreement with the residence time in the dead volume of the bypass (0.35 ml), given the fact that the flowrate was 0.5 ml/min. The response time (the moment at which 95% of final signal was reached) differed significantly for three gases (Figs. 2a–2c) and increased in the order $H_2 < \mathrm{Ar} < O_2$. Probably, this is at least partly caused by differences in the diffusivity of the gases in the membrane; $D_{\mathrm{eff}}$ for hydrogen, argon and oxygen are $1.0 \times 10^{-9}$, $2.0 \times 10^{-9}$ and $3.0 \times 10^{-9}$ m$^2$/s, respectively [20,21] but this can only partly explain the observed effect. Therefore adsorption of gases, and especially O$_2$, in the membrane probably contributes to the delay time.

One important cause of the long response time could be the thickness of our membrane (200 µm). Much faster response (typically 0.3 min) was reported by Kostainen et al. [22] for organic compounds (VOC's) dissolved in water, applying a similar configuration using a much thinner membrane (25 µm). Unfortunately, thinner membranes cannot be used in our set-up because of mechanical instability, inducing leakage of water into the vacuum system.

Anyhow, the relative slow response of the detector implies that real time concentrations cannot be monitored reliably in transient experiments. We will show later that calibration of integral pulses is possible and reliable though.

### 3.3. *Reactor behavior and spreading of the response to the pulse*

The responses to an argon pulse with different configurations are represented in Fig. 3. The most obvious difference is the change in delay times. In the case of the by pass and the reactor with CNF, delay times of 0.7 and 3.0 min can be fully accounted for based on the dead volumes of the bypass (0.35 ml) and the reactor with CNF (1.5 ml), taking into consideration a flow rate of 0.5 ml/min. The experimental delay times of the empty reactor (4.2 min) and the reactor with silica (1.7 min) differ slightly from theoretical estimations of the residence times, based on the dead volumes (1.90 and 0.70 ml respectively, resulting in 3.8 and 1.4 min respectively); the

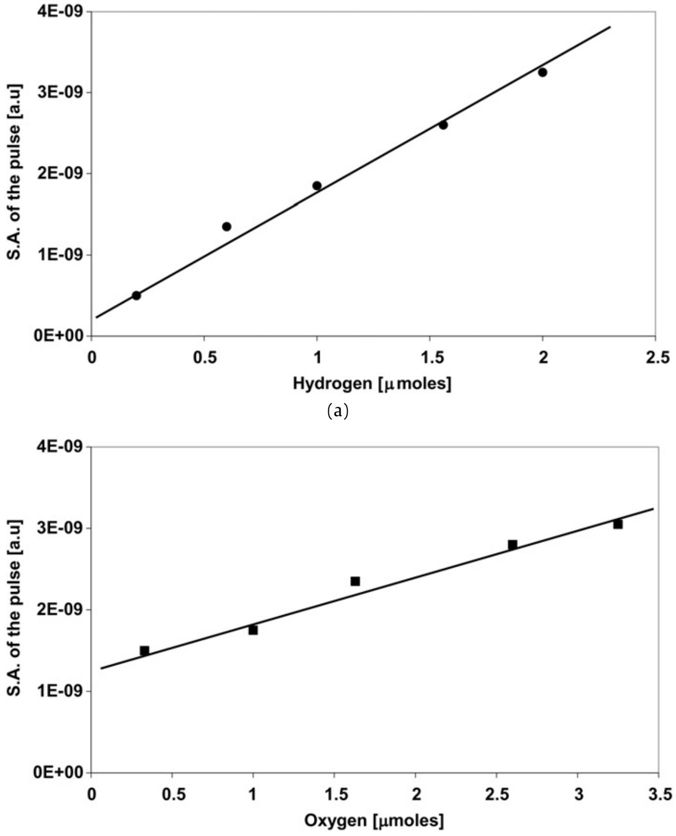
**Table 1**
Catalyst loadings and dispersions determined in gas phase and in liquid phase

| Catalyst | Loading (wt%) | $D_{Gas}$(H/Pt) gas phase chemisorption | Amount of Pt in reactor | | H/Pt-TEM[a] | $(H_2)_{liquid}$ (µmol) | $(O_2)_{liquid}$ (µmol) | $D_{liquid}(H/Pt)$[b] |
|---|---|---|---|---|---|---|---|---|
| | | | Bulk (µmol/g) | Surface (µmol) | | | | |
| EuroPt-1 | 6.3 ± 0.05 | 0.65 | 323 | 10.5 | – | 16 | 8.5 | 0.66 |
| Pt/CNF | 3.0[c] | 0.25 | 154 | 11.2 | 0.29 | 17 | 9.2 | 0.25 |
| $Pt/SiO_2$[c] | 1.0 ± 0.05 | 0.61 | 51 | 8.8 | 0.54 | 12 | 7 | 0.56 |

[a] Calculated based on: $D(\text{TEM}) = \frac{1.08}{d(\text{nm})}$ [18].

[b] Dispersion in liquid phase ($D_L$) based on: $D_{liquid} = \frac{2^*(H_2)L}{(\text{Bulk(Pt)})^* W_{cat}}$.

[c] The Pt loading assumed based on preparation procedure.



(a)

(b)

**Fig. 4.** (a) Hydrogen ($m/z$ 2) calibration curve based on a surface area of the pulse (5 min pulse, $F = 0.5$ ml/min, $c = 0.078$–$0.78$ mM, $T = 295$ K), $R^2 = 0.99$. (b) Oxygen ($m/z$ 32) calibration curve based on a surface area of the pulse (5 min pulse, $F = 0.5$ ml/min, $c(O_2) = 0.13$–$1.3$ mM, $T = 295$ K), $R^2 = 0.98$.

estimations of the dead volumes are apparently slightly inaccurate. Furthermore, the differences in the shapes of the break-through curves are modest, indicating that hydrodynamics are quite similar for all cases, despite significant differences in pressure drop, varying between 2 and 40 bars for the CNF support and the fixed bed of HPLC silica, respectively.

The response to a glucose pulse of CNF/Ni foam reactor presented in part 1 of this paper showed even more distortion of the pulse-shape, which was explained with significant reversible adsorption of glucose on the CNF support. The experimental result with Ar supports this interpretation by demonstrating less peak distortion using a species that certainly does not adsorb (Ar).

### *3.4. Calibration of the analyzer in pulse-mode*

The calibration curves presented in Figs. 4a and 4b show a linear relationship between the amount of hydrogen and oxygen present in a single pulse with the surface area of the peak obtained in a blank experiment. The amount of dissolved gas present was varied via the concentration. This result is not trivial when taking in consideration that the response of the analyzer is relatively slow, especially for oxygen, as discussed before. Apparently, the delays in the rising part and the declining part of the peak compensate each other. Comparable results were obtained for Ar and $N_2$ (not shown), demonstrating that the method can be generally applied for dissolved gasses. Also, the presence of a second dissolved component does not significantly influence the calibration (<2%). The calibration curve does not go through zero in Fig. 4a; at the moment there is no satisfying explanation for this phenomenon.

The smallest amount of hydrogen and oxygen that can be quantitatively determined is in the order of 0.1 and 0.3 µmol respectively. Calibrations were done before and after titration experiments, resulting in reproducible data within 10% experimental error.

### *3.5. $O_2$ and $H_2$ titration in aqueous solution*

Fig. 5 a shows the result of pulsing hydrogen on pre-oxidized EuroPt-1 as well as on silica only (blank). Consumption of hydrogen on silica was not observed. However, complete consumption of hydrogen is observed during the first seven pulses on the oxidized EuroPt-1. A gradual breakthrough occurs during the next four pulses. Finally, the surface areas of the peaks become identical to the blank experiment, despite the difference in peak shape, which will be discussed later, indicating that hydrogen is not consumed anymore. The total amount of hydrogen consumed was 16 µmol, applying the calibration curve in Fig. 4a.

Two subsequent oxygen pulses (Fig. 5b) are completely consumed, followed by a gradual breakthrough during the 3rd and 4th pulse. Next, the response stabilized and became equal to the response in the blank experiment. The total amount of oxygen consumed is 8.5 µmol, using the calibration curve in Fig. 4b. The same experiments were performed with Pt/CNF and $Pt/SiO_2$ (not shown) and the total amounts of hydrogen and oxygen consumed with Pt/CNF and $Pt/SiO_2$ catalyst were 17 µmol $H_2$/9.2 µmol $O_2$ and 12 µmol $H_2$/7 µmol $O_2$, respectively (Table 1).

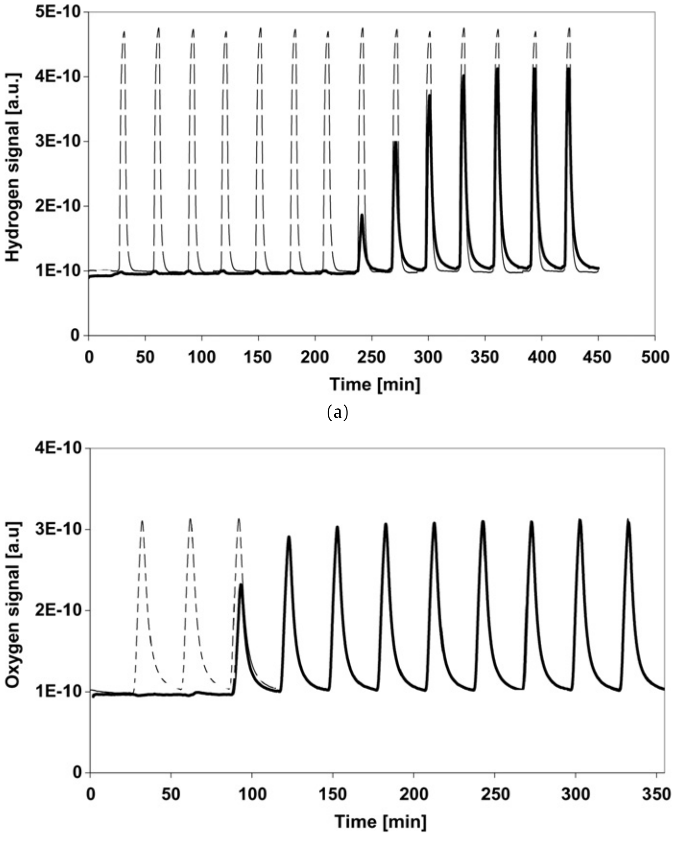
The amount of hydrogen consumed in the titration experiment with EuroPt-1 (16 µmol) is almost 3 times the amount of pre-adsorbed oxygen (5.3 µmol), in agreement with the following assumptions:

1. two hydrogen atoms react with one pre-adsorbed oxygen atom ($O_a$) to form water and one hydrogen atom would subsequently adsorb on platinum (Eq. (3.1)),

$$3H_2 + 2Pt_s\text{–}O_a \rightarrow 2H_2O + 2Pt_s\text{–}H_a, \tag{3.1}$$

2. adsorption stoichiometry of O on Pt is one,
3. adsorption stoichiometry of H on Pt is one.

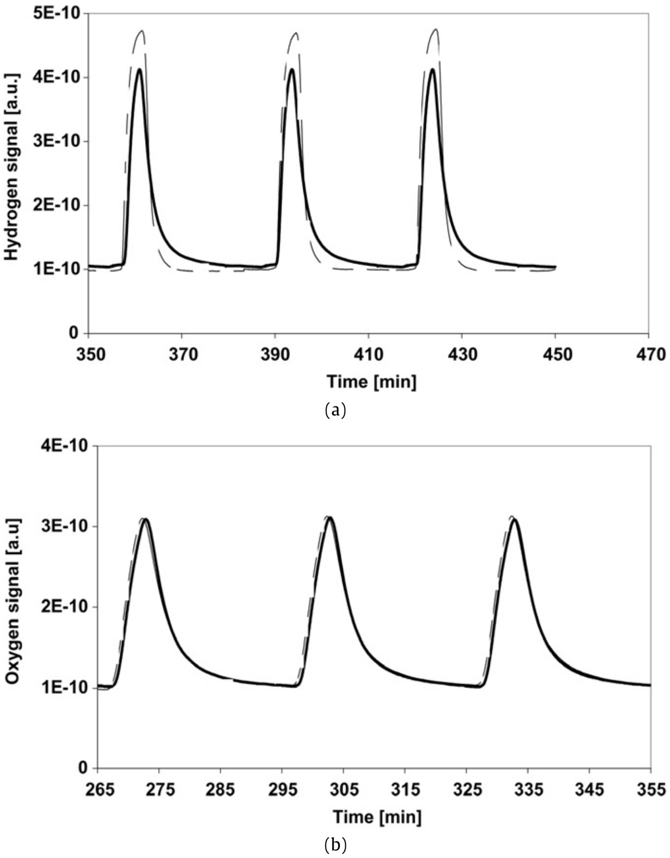
In the following experimental sequence, the amount of oxygen consumed in the titration experiment (8.5 µmol) agrees well with



(a)

(b)

**Fig. 5.** (a) Titration of pre-adsorbed oxygen on EuroPt-1 using water saturated with hydrogen (2.5 mL pulse, $F = 0.5$ ml/min, $c(H_2) = 0.78$ mM, $T = 295$ K). (—) $H_2$–$O_2$ titration; (– – –) Blank experiment. (b) Titration of pre-adsorbed hydrogen on EuroPt-1 catalyst using water saturated with oxygen (2.5 mL pulse, $F = 0.5$ ml/min, $c(O_2) = 1.3$ mM, $T = 295$ K). The experiment was done immediately after the titration with hydrogen; (—) $O_2$–$H_2$ titration; (– – –) Blank experiment.



(a)

(b)

**Fig. 6.** (a) Details of the last three pulses using water saturated with hydrogen on EuroPt-1 catalyst after the titration of pre-adsorbed oxygen has been completed (2.5 mL pulse, $F = 0.5$ ml/min, $c(H_2) = 0.78$ mM, $T = 295$ K); (—) $H_2$–$O_2$ titration; (– – –) Blank experiment. (b) Details of the last three pulses using water saturated with oxygen on EuroPt-1 catalyst after the titration of pre-adsorbed hydrogen has been completed (2.5 mL pulse, $F = 0.5$ ml/min, $c(O_2) = 1.3$ mM, $T = 295$ K), (—) $O_2$–$H_2$ titration; (– – –) Blank experiment.

the amount of oxygen that would be consumed (8.0 μmol) if one oxygen atom would react with two pre-adsorbed hydrogen atoms ($H_a$) to form water and one oxygen atom would subsequently adsorb on platinum like (Eq. (3.2))

$$1.5O_2 + 2Pt_s\text{–}H_a \rightarrow H_2O + 2Pt_s\text{–}O_a. \tag{3.2}$$

Thus, hydrogen–oxygen titration results in liquid phase for the EuroPt-1 catalyst agree well with the gas phase titration stoicheometry reported by Benson et al. [14] in Eq. (3.1). Ratios between the amounts of oxygen and hydrogen consumed in titration experiments for all three catalysts are, within experimental error, close to 2, as would be expected from Eqs. (3.1) and (3.2). More importantly, the platinum dispersions obtained in liquid phase are in excellent agreement with dispersions based on hydrogen chemisorption in gas phase, for all three catalysts as shown in Table 1.

The minimal amount of hydrogen that can be detected in a single pulse is 0.1 μmol $H_2$. This amount is equivalent to approximately 0.7% of a pre-adsorbed oxygen monolayer on EuroPt-1 catalyst, which is equivalent to about 0.5 $m^2$ Pt surface. The sensitivity thus obtained is similar to the method of Kiraly et al. [8], titrating with $CS_2$. An obvious advantage of the $H_2$–$O_2$ titration method is that it is in principal not destructive because no irreversible adsorption is taking place, in contrast to the $CS_2$ method. The advantage of our method as compared to the $H_2$–$O_2$ titration results of Bradley et al. [17] is robustness by avoiding volumetric methods, needing extremely accurate temperature control. Anyhow, our data support the result of Bradley et al. [17] and disagree with the observations of Kiraly et al. [16], in the sense that no significant influence of solvent (i.e. water) on chemisorption of hydrogen and oxygen on precious metals was found, and consequently no effect exists on the dispersion. This is not in agreement with the result of Kiraly et al. [16] claiming different dispersions of Pt on $Al_2O_3$ catalyst when measured in gas phase versus methanol. However, it is not possible to rule out that this effect is due to different adsorption stoicheometries for $H_2$ in gas phase versus $CS_2$ in methanol.

Fig. 6a provides a detailed comparison of the shape of the signals of dissolved hydrogen when pulsing over silica versus pulsing over EuroPt-1, after the titration of adsorbed oxygen was completed (i.e. the last pulses in Fig. 5a). The peak broadening in Fig. 6a clearly indicates that a weak but significant reversible interaction is taking place between dissolved $H_2$ and a hydrogen covered platinum surface. This reversible interaction must take place on the Pt surface because no such effect is observed with silica only. In contrast, Fig. 6b, showing details of the last pulses in Fig. 5b when the titration of pre-adsorbed hydrogen has been completed, shows no significant influence of the platinum on the peak shape of oxygen. Similar results were obtained with Pt/$SiO_2$ and Pt/CNF.

This result shows that the technique developed here can provide unique information on the influence of solvent (water in this case) on reversible interactions of dissolved species with catalyst surfaces. It is well known that charge separation on an oxidized Pt surface is much larger than on a H-covered Pt surface, because of the significant larger difference in electron affinity between O and Pt versus H and Pt. As a result, more charge separation on the oxidized surface renders a more hydrophilic platinum surface and a-polar $O_2$ molecules are not likely to interact. The charge separation on the H-covered surface is much less, the surface will be less hydrophilic and $H_2$ molecules could well interact, as observed in Fig. 6a. In fact, $H_2$ molecules will prefer the relatively a-polar H-covered Pt surface over solvatation with highly polar water molecules. An alternative explanation would be that $H_2$ dissociative chemisorption is reversible under the conditions applied in this study, whereas $O_2$ chemisorption is apparently irreversible. Anyhow, unique information on reversible versus irreversible adsorption is obtained.

We also observed ageing phenomena during subsequent experiments. When repeating $H_2$–$O_2$ titrations with Pt/$SiO_2$ catalyst three times, a decrease of the hydrogen and oxygen uptake in subsequent titrations was observed. In addition, XRF analysis of the Pt/$SiO_2$ catalyst after the titration experiments showed a decrease of the Pt loading (from 1.0 to 0.87 wt%); apparently some platinum is lost during the experiments. Hydrogen chemisorption of the Pt/$SiO_2$ catalyst after the titration experiments showed a decrease of the Pt dispersion (from 0.61 to 0.53).

It can be speculated that these effects are due to dissolution of the smallest metal particles during the titration sequence, as this would account for both the loss of Pt as well as the decrease in dispersion. However, we cannot rule out $H_2$ induced ageing, as reported by Douidah et al. [23] for silica-supported platinum particles in aqueous media under hydrogen atmosphere.

The relevant point here, however, is the fact that this result demonstrates the ability of the methods described, to observe changes in the characteristics of catalyst in liquid phase without the necessity to remove the aqueous phase. Another advantage is non-destructive testing, i.e. catalyst does not need to be removed from the reactor, which is especially an advantage in case of (micro-) structured reactors and micro-reactors because catalysts are not easily removable. Also, the sensitivity of detection is useful for characterization of micro-fluidic catalytic devices and future work will be in this direction.

Finally, it is demonstrated that quantitative evaluation of pulse experiments in the range of minutes is possible. Thus, transient experiments consuming or producing dissolved gasses can be monitored quantitatively as long as the typical width of the signals is comparable. However, the ESI-MS detector is responding within a few seconds [1]; when using both detectors, experimental design needs to consider the response times of both detectors. Thus, application of the detector discussed here will limit the window of operation of the complete set-up and future work will include testing membrane materials and thinner membranes, aiming at faster response for improved applicability of the method. On the other hand, it is obvious that the most relevant gasses for liquid phase catalysis, i.e. hydrogen and oxygen for hydrogenation reactions and oxidation reaction respectively, can be detected, as well as $N_2$ which would be important for studying hydrogenation of nitrite and nitrate. In fact, it is reasonable to assume that most gasses can be detected because effective diffusion coefficients will in general not very more than in this study. On the other hand, membrane materials should be selected that minimize adsorption of the relevant gasses.

We have demonstrated application in aqueous phase; in principle application in organic phase is also possible by selecting compatible membrane materials. However, it should be pointed out that changing the solvent from water to an organic solvent would also imply tuning of the ESI-MS as discussed in part 1, as well as ensuring compatibility of all parts of the equipment with the solvent, e.g. pumps, sealings and tubings. Obviously, this can be done but will require a significant effort.

## 4. Conclusions

We have, for the first time, successfully applied an analyzer for gasses dissolved in water, based on membrane inlet mass spectrometry (MIMS), for in-line detection in the exit of a catalytic reactor in a transient experiment. The technique was applied for determination of the dispersion of platinum supported catalyst in the aqueous phase via $H_2$–$O_2$ titration. The titration stoichiometries obtained in liquid phase for the 3 different catalysts (EuroPt-1, Pt/$SiO_2$ and Pt/CNF) agree well with the gas phase titration stoichiometry reported in literature. The platinum dispersions obtained in liquid phase are in excellent agreement with dispersions based on hydrogen chemisorption in gas phase for all three catalysts and we conclude that water has no influence on the actual dispersion of Pt and on the stoichiometry of adsorption. Despite the relatively slow dynamic response of the detector, it was proven possible to perform quantitative experiments in pulse mode. The capability of this method is further demonstrated by the surprising observation that dissolved hydrogen physisorbs significantly on a reduced Pt catalyst whereas dissolved oxygen does not interact with an oxidized catalyst.

## Acknowledgments

The authors thank, Ing. L. Vrielink for XRF and BET analysis, Ing. M. Smithers for TEM measurements, Ing. A. Hovestad for assistance with reactors preparation, Ing. A. Wonders (University of Eindhoven), Ing. J. Spies and Ing. B. Geerdink for technical assistance, Dr. J. Kromkamp and J. Peene (NIOO-KNAW) for discussions on MIMS. Financial support for the project (TPC 5694) by STW (The Netherlands) is kindly acknowledged. This work was performed under the auspices of NIOK.

## References

[1] D. Radivojević, M. Ruitenbeek, K. Seshan, L. Lefferts, J. Catal. 257 (2008) 244.
[2] http://www.orbisphere.com, last accessed on 12 February 2008.
[3] M. Meyberg, F. Roessler, Ind. Eng. Chem. Res. 44 (2005) 9705.
[4] O. Wolter, J. Heitbaum, B. Bunsenges, Phys. Chem. 88 (1984) 2.
[5] G.E. Dima, A.C.A. de Vooys, M.T.M. Koper, J. Electroanal. Chem. 15 (2003) 554.
[6] T.M. Kana, C. Darkangelo, M.D. Hunt, J.B. Oldham, G.E. Bennett, J.C. Cornwell, Anal. Chem. 66 (1994) 4166.
[7] R. Kostiainen, T. Kotiaho, I. Mattila, T. Mansikka, M. Ojala, R.A. Ketola, Anal. Chem. 70 (1998) 3028.
[8] U.K. Singh, M.A. Vannice, Appl. Catal. A 213 (2001) 1.
[9] T. Mallat, A. Baiker, Catal. Today 19 (1994) 247.
[10] J.M.H. Dirkx, H.S. van der Baan, J. Catal. 67 (1981) 1.
[11] G.C. Bond, P.B. Wells, Appl. Catal. 18 (1985) 221.
[12] G.C. Bond, P.B. Wells, Appl. Catal. 18 (1985) 224.
[13] C.R. Adams, H.A. Benesi, R.M. Curtis, R.G. Meisenheimer, J. Catal. 1 (1962) 336.
[14] T.E. Whyte Jr., Catal. Rev. 8 (1974) 117.
[15] J.E. Benson, M. Boudart, J. Catal. 4 (1965) 704.
[16] Z. Kiraly, A. Mastalir, A. Csaszar, H. Demir, D. Uner, G.H. Findenegg, J. Catal. 245 (2007) 267.
[17] J.S. Bradley, W. Busser, Catal. Lett. 63 (1999) 127.
[18] C.H. Bartholomew, R.J. Farrauto, Fundamentals of Industrial Catalytic Processes, second ed., Wiley–Interscience, 2006, p. 146.
[19] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, CRC Press, 1998–1999, pp. 8–86.
[20] M.-B. Hägg, J. Membr. Sci. 170 (2000) 173.
[21] L. Brandão, L.M. Madeira, A.M. Mendes, J. Membr. Sci. 288 (2007) 112.
[22] R. Kostainen, T. Kotiaho, I. Mattila, T. Mansikka, M. Ojala, R.A. Ketola, Anal. Chem. 70 (1998) 3028.
[23] A. Douidah, P. Marécot, J. Barbier, Appl. Catal. A 225 (2002) 11.
[24] A. M Chaparro, N. Mueller, C. Atienza, L. Daza, J. Electroanal. Chem. 591 (2006) 69.
[25] P.M. Vignais, L. Cournac, E.C. Hatchikian, S. Elsen, L. Serebryakova, N. Zorin, B. Dimon, Int. J. Hydrogen Energy 27 (2002) 1441.