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Published in: CATALYSIS SCIENCE & TECHNOLOGY

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Correction for a possible reversible adsorption over the “inert” material

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Abstract
All TAP micro-reactor configurations contain inert particles which are used so that the catalyst zone can be maintained under isothermal conditions. Even on “inert” particles adsorption will occur to some degree; however, the extent to which this occurs has a critical influence on the analysis of the TAP data. In many cases the assumption that there is no interaction between probe molecules and inert particles is required as reversible adsorption over inert material is problematic when the TAP model has to be solved. Moreover, as the TAP pulse response experiments are designed to be conducted within the Knudsen diffusion regime, central to TAP data analysis is the characterization of the diffusional transport of reagent molecules through the micro-reactor, which is achieved via “diffusion only” experiments over an inert one zone packing. Therefore, if there are any processes occurring in addition to Knudsen diffusion over the inert material, such as reversible adsorption, it is important to factor these into the analysis. If these additional processes are not included, the entire data analysis would be questionable. The current work discloses the development a function which accounts for the adsorption over the inert material, so that the TAP data analysis can be accurately determined. This newly developed analysis method has been exemplified using the selective reduction of oxygen in a hydrogen rich ethylene feed over silver catalysts as a case study.
Introduction

The Temporal Analysis of Products (TAP) reactor system has been designed for detailed kinetic characterization of various heterogeneous catalysts in the gas phase (Gleaves et al. 1988, 1997). The technique has been successfully applied to a wide range of reactions and catalysts (Gleaves et al., 1988, 1997; Goguet et al. 2006, 2010; Keipert and Baerns, 1998; Morgan et al., 2010; Olea et al., 2001; Pérez-Ramírez and Kondratenko, 2007; Shekhtman et al. 2008; Yablonsky et al., 2003). The TAP reactor operates on the premise of injecting a small gas pulse of very short duration into an evacuated micro-reactor containing a packed bed of particles. The duration of the inlet pulse is of the order of 250-500 µs, which provides the technique with a sub-millisecond time resolution. When the number of molecules in the pulse is sufficiently small ($\approx 10^{-10}$ moles), the convective flow disappears and gas transport occurs by Knudsen diffusion. Due to the low inlet pulse intensity, the pulse-response TAP experiment provides an opportunity to control the catalyst composition (Gleaves et al., 1997). In a single-pulse TAP experiment, the changes in the catalyst composition during the experiment is very small compared with the amount of surface active sites due to the small pulse intensity. In a multi-pulse TAP experiment, the catalyst composition can be changed gradually, in a well-controlled manner.

It is common practice when packing the TAP micro-reactor for kinetic catalyst characterization that the catalyst (active) zone is sandwiched between zones which are packed with inert material. The key advantage of such a reactor configuration is that it significantly improves temperature uniformity in the catalyst zone. In the case of the TAP technique this is known as a three-zone TAP reactor configuration. A limiting case of the three-zone configuration is a more advanced thin-zone TAP reactor (TZTR) configuration where the length of the active zone is much smaller than the length of the inert zones. The TZTR allows maintenance of nearly uniform concentration profiles in the thin catalyst zone during the vacuum pulse-response TAP experiment (Shekhtman et al., 1999).

Typical choices of inert material include silicon-carbide and quartz, with particles of approximately the same size as the catalyst. These materials typically have small surface area per volume compared with the catalyst under investigation and, therefore,
are assumed to make little contribution to the adsorption processes. This assumption that
there is no interaction between probe molecules and inert particles is critical in modelling
TAP data (or data from any other transient experiments). Typically, this assumption is
justified in a separate blank experiment. In TAP studies, such experiments involve
pulsing various probe molecules over the reactor packed with inert material at various
temperatures. Then, the responses are compared with theoretical curves calculated from
the one-zone TAP Knudsen diffusion model. This model implies that the only process
that takes place in the reactor is Knudsen diffusion. It is important to note that simple
curve fitting of a few responses is not sufficient justification of Knudsen diffusion. It is
well known that when adsorption/desorption are fast compared to the characteristic
diffusion time, there is a contribution of the adsorption/desorption to the response shape.
The contribution of fast adsorption/desorption appears as if the response corresponds to
diffusion with a smaller diffusivity. Thus, an important part of the test for Knudsen
diffusion is checking if observed diffusivities ($D$) or residence times ($\tau_{res}$) follow the
Knudsen diffusion law:

$$D \propto \sqrt{M_w} \left( \frac{T}{\tau_{res}} \right)$$

(1)

The correct dependence of the Knudsen diffusivity or residence time on
temperature ($T$) and molecular weight ($M_w$) of probe molecules can justify that none of
probe molecules interact with the tested inert material in the studied temperature range.
Figure 1 reports the correct dependence for helium, neon, nitrogen and argon in the
temperature range 50-300 °C over silicon carbide (particle size 500 µm). However, not
all inert one-zone TAP tests produce such a clear dependence.

There are four important factors that limit the inert behaviour of “inert material”
in the pulse-response TAP experiment:

1. Very active molecules (e.g. ammonia or NOX) tend to adsorb on most
surfaces;
2. In the low temperature range physical adsorption may be sufficiently strong to increase the residence time of the molecules to that comparable with the characteristic time of Knudsen diffusion (0.01-0.1 s);

3. Although surface impurities on the inert particles may be low compared with the number of active sites on the catalyst, a typical TAP pulse only contains a very small amount of molecules compared with number of catalyst active sites. Hence, the quantity of impurities and number of pulsed molecules may be comparable.

4. Catalyst pre-treatment or activation using normal pressure flows often precedes kinetic tests. Such normal pressure treatments may significantly increase or activate the surface impurities on the inert particles.

Reversible adsorption (likely physical adsorption) is the most typical process that occurs on “inert” surfaces.

In this paper, theoretical tools to account for the reversible adsorption over “inert” particles in pulse-response TAP experiments and demonstration of the tools in practice are presented. First, the adsorption properties of the inert material are characterized in a series of one-zone TAP experiments. Second, the studied inert material is used for the thin-zone TAP reactor (TZTR) configuration, which includes catalyst and inert material (Shekhtman et al., 1999). The theoretical tools allow the extraction of quantitative kinetic information about the interaction between probe molecules and catalyst in the form of basic kinetic coefficients (Shekhtman et al., 2003). These basic kinetic coefficients were introduced previously as primary kinetic characteristics observed in the TAP experiment (Shekhtman et al., 2003, 2007).

In the TZTR, the concentration non-uniformity in the catalyst zone is negligible for a wide range of TAP conditions (Shekhtman et al., 2005). These conditions are achieved when the length of the catalyst zone (or amount of catalyst) is much smaller than length of the inert zones (amount of inert material). Hence, the amount (or volume) of inert material in the reactor is much greater than the amount of catalyst compared to the typical three-zone case. Thus, the adsorption over the inert material would produce a
relatively greater contribution in the case of the TZTR, which makes the problem of reversible adsorption over the inert especially relevant for this TAP reactor configuration.

**One-zone model with reversible adsorption**

The model of a single-pulse TAP experiment in a one-zone reactor can be expressed by a system of two partial differential equations for gas and surface concentrations (Gleaves et al., 1997):

\[
\frac{\partial C_g}{\partial t} = D \frac{\partial^2 C_g}{\partial x^2} - k_a C_g + k_d C_\theta 
\]

\[
\frac{\partial C_\theta}{\partial t} = k_a C_g - k_d C_\theta 
\]

where: \( \varepsilon \) is the bed voidage; \( C_g \) and \( C_\theta \) are the gas and surface concentrations normalized per unit of reactor volume, respectively; \( D \) is the Knudsen diffusivity; \( x \) is reactor axial coordinate; \( k_a \) is a global adsorption rate constant (1/s); \( k_d \) is a desorption rate constant (1/s).

Equations (2) and (3) subject to the ideal TAP initial and boundary conditions (Constales et al., 2006):

**Zeroth initial condition:**
\[
C_g \bigg|_{t=0} = 0, \quad C_\theta \bigg|_{t=0} = 0
\]

**Vacuum condition at the exit:**
\[
C_g \bigg|_{x=L_r} = 0,
\]

**Narrow inlet pulse:**
\[
-A_r D \frac{\partial C_g}{\partial x} \bigg|_{x=0} = 2N_g \delta(t)
\]

where: \( A_r \) is a reactor cross-section area; \( D_{in} \) is the Knudsen diffusivity in the inert zone; \( L_r \) is the length of the whole reactor and \( N_g \) is the number of molecules in the inlet pulse.
The one-zone model can be solved using the Laplace transformation method, as detailed elsewhere (Gleaves et al., 1997). The Laplace solution for the exit flow time dependence ($F_{exit}$) observed in the pulse response TAP experiment was found as:

$$F_{exit}(s) = \frac{1}{Cosh\left(2\tau_{in} s \left(1 + \frac{k_a}{\varepsilon(s + k_d)}\right)\right)}$$ \hspace{1cm} (7)

where the residence time in the inert one zone ($\tau_{in}$) is given by: $\tau_{in} = \frac{\varepsilon_m L_r}{2D_m}$ and $s$ is the Laplace transform variable.

The Laplace solution (7) can be used to calculate moments ($M_n$) of the exit flow responses ($F_{exit}$) from the following equation:

$$M_n = \int_0^{\infty} t^n F_{exit}(t) dt = (-1)^n \left| \frac{\partial^n F_{exit}(s)}{\partial s^n} \right|_{s=0}$$ \hspace{1cm} (8)

From Equation (8), the following expressions for moments of exit flow were determined:

$$M_{0}^{1Z} = 1; \hspace{1cm} (9)$$

$$\frac{M_{1}^{1Z}}{M_{0}^{1Z}} = \tau_{in} \left(1 + \frac{k_a}{\varepsilon k_d}\right)$$ \hspace{1cm} (10)

$$\frac{M_{2}^{1Z}}{M_{0}^{1Z}} = \frac{5}{3} \frac{M_{1}^{1Z^2}}{M_{0}^{1Z^2}} = \frac{\tau_{in} k_a}{\varepsilon k_d^2}$$ \hspace{1cm} (11)

where the upper index “1Z” denotes the moments measured in the inert one-zone TAP reactor. Equation (9) indicates that no conversion occurs in this case. Both Equations (10) and (11) can be used to determine the adsorption and desorption rate constants for an
inert material from the moments of responses observed in the one-zone TAP experiment. They can also be used to calculate the following parameters:

\[
\frac{k_a}{\varepsilon k_d} = \frac{M_1^{1Z}}{\tau_m M_0^{1Z}} - 1 \quad (12)
\]

\[
\frac{k_a}{\varepsilon k_d^2} = \frac{1}{\tau_m} \left( \frac{M_2^{1Z}}{M_0^{1Z}} - \frac{5}{3} \frac{M_1^{1Z^2}}{M_0^{1Z^2}} \right) \quad (13)
\]

The ratios \( \frac{k_a}{\varepsilon k_d} \) and \( \frac{k_a}{\varepsilon k_d^2} \) are explicitly present in the thin-zone solutions, as is discussed in the following section.

**Thin-zone model with reversible adsorption over inert particles**

The thin zone TAP reactor model includes partial differential equations for the inert zones and algebraic equations for matching the inert zone solutions in the centre of the catalyst zone (\( L_{TZ} \)). The mass balance in the inert zones is described by equations (2) and (3) from the previous section, which include the same diffusion, adsorption and desorption terms. The thin-zone matching conditions for the inert zone solutions (\( C_I \) and \( C_{II} \)) can be written as shown in equations (14) and (15) (Shekhtman et al., 2004):

\[
C_I(t)_{x=L_{TZ}} - C_{II}(t)_{x=L_{TZ}} = 0 \quad (14)
\]

\[
-A_r D \frac{\partial C_I}{\partial x} \bigg|_{x=L_{TZ}} + A_r D \frac{\partial C_{II}}{\partial x} \bigg|_{x=L_{TZ}} = A_r L_{cat} R_{TZ} (t) \quad (15)
\]

where \( L_{TZ} \) is the axial position of the middle of the thin zone; \( L_{cat} \) is the length of the catalyst zone and \( R_{TZ} \) is the spatial average reaction rate in the thin zone.

Equation (14) ensures the continuity of concentration and is not related to conversion or reaction rate (Shekhtman et al., 2004). In general, the reaction rate for any reaction is taken into account in Equation (15), i.e. the difference between diffusional
flows in/out of the thin zone is equal to the reaction rate (Shekhtman et al., 2004). Thus the solutions that are presented (see Equations (17), (18) and (19)) describe all possible reactions between a probe molecule and catalyst.

The presented thin-zone model can be solved using the Laplace transformation method, subject to the initial and boundary conditions (4-6). The Laplace solution for the exit flow was found as:

\[
\bar{F}_{\text{exit}}(s) = \frac{1}{\cosh\left(\sqrt{2\tau_{\text{in}} s \left(1 + \frac{k_a}{\epsilon (s + k_d)}\right)}\right) + \frac{r(C_{CS}, s)\tau_{\text{cat}} \sinh\left(\sqrt{2\tau_{\text{in}} s \left(1 + \frac{k_a}{\epsilon (s + k_d)}\right)}\right)}{\sqrt{2\tau_{\text{in}} s \left(1 + \frac{k_a}{\epsilon (s + k_d)}\right)}}}
\]  

(16)

where \( r(C_{CS}, s) \) is the Laplace reactivity that linearly relates the rate and the corresponding gas concentration in the Laplace domain (Shekhtman et al., 2003). The residence time in the catalyst (\( \tau_{\text{cat}} \)) zone is given by: \( \tau_{\text{cat}} = \frac{L_r L_{\text{cat}}}{2D} \)

Using equations (8) and (16), the following expressions for moments of exit flow were determined:

\[
M_{0}^{TZ} = \frac{1}{1 + \tau_{\text{cat}} r_0}
\]

(17)

\[
\frac{M_{1}^{TZ}}{M_{0}^{TZ^2}} = \tau_{\text{cat}} r_1 + \tau_{\text{in}} \left(1 + \frac{\tau_{\text{cat}} r_0}{3}\right) \left(1 + \frac{k_a}{\epsilon k_d}\right)
\]

(18)

\[
\frac{M_{2}^{TZ}}{M_{0}^{TZ^2}} = -2 \frac{M_{1}^{TZ}}{M_{0}^{TZ^3}} = -2\tau_{\text{cat}} r_2 - \frac{\tau_{\text{in}}^2}{3} \left(1 + \frac{\tau_{\text{cat}} r_0}{5}\right) \left(1 + \frac{k_a}{\epsilon k_d}\right)^2 - \frac{2\tau_{\text{in}}}{3} \left(\tau_{\text{cat}} r_1 \left(1 + \frac{k_a}{\epsilon k_d}\right) - \frac{k_a}{\epsilon k_d} \left(\tau_{\text{cat}} r_0' + 3\right)\right)
\]

(19)
where $r_0$, $r_1$ and $r_2$ are basic kinetic coefficients (s$^{-1}$).

Here, the upper index “TZ” denotes the moments that were measured in the thin-zone TAP reactor. In the case when no conversion occurs in the catalyst zone, equations (17), (18) and (19) can be simplified as:

$$M_0^{TZ} = 1;$$

$$rac{M_1^{TZ}}{M_0^{TZ}} = \tau_{cat}r_1 + \tau_m\left(1 + \frac{k_a}{\varepsilon k_d}\right)$$

$$rac{M_2^{TZ}}{M_0^{TZ}} = -2\tau_{cat}r_2 + \frac{\tau_{cat}^2 r_1^2}{3} + \frac{2k_a \tau_m}{\varepsilon k_d^2}$$

Here, the basic kinetic coefficients $r_0$, $r_1$ and $r_2$ describe the catalyst [8], while the parameters $k_a$ and $k_d$ characterize adsorption/desorption over the inert material. The rate constants $k_a$ and $k_d$ are both present in equations (17) to (22) in the form of either ratio $\frac{k_a}{\varepsilon k_d}$ or $\frac{k_a}{\varepsilon k_d^2}$. The first and second moments observed in one-zone experiment explicitly determine these ratios (equations (10) to (13)). Consequently, in order to analyze thin-zone data, the ratios $\frac{k_a}{\varepsilon k_d}$ and $\frac{k_a}{\varepsilon k_d^2}$ should merely be determined in one-zone test, using equations (12) and (13).

In particular, combining Equation (12) with Equation (21) and Equation (13) with Equation (22), it is possible to determine $r_1$ and $r_2$ respectively, in a step by step manner. Firstly, $r_1$ can be calculated from Equation (23), using Equations (12) and (21):

$$\tau_{cat}r_1 = \frac{M_1^{TZ}}{M_0^{TZ}} - \frac{M_1^{1Z}}{M_0^{1Z}}$$

$$\frac{M_2^{TZ}}{M_0^{TZ}} - \frac{5}{3} \frac{M_1^{TZ}}{M_0^{TZ}} = -2\tau_{cat}r_2 + \frac{\tau_{cat}^2 r_1^2}{3} + \frac{2k_a \tau_m}{\varepsilon k_d^2}$$

9
Then $r_2$ can be calculated using equations (13) and (22):

$$
|\tau_{\text{cat}}r_2| = \frac{M_2^{TZ}}{2M_0^{TZ}} - \frac{5 M_1^{TZ^2}}{6 M_0^{TZ^2}} \tau_{\text{cat}} r_1^2 - \frac{M_2^{1Z}}{M_0^{1Z}} - \frac{5 M_1^{1Z^2}}{3 M_0^{1Z^2}}
$$

Equations (23) and (24) are then applied to the experimental data.

**Application to the experimental data analysis: A case study with the selective reduction of oxygen in a hydrogen-rich ethylene feed over 2% Ag/γ-Al$_2$O$_3$ catalyst**

This correction function has been utilised for TAP studies of the selective reduction of oxygen in a hydrogen-rich ethylene feed over a 2% Ag/γ-Al$_2$O$_3$ catalyst, which have been extensively characterised previously (Inceesungvorn et al., 2008, 2010; Inceesungvorn 2009). High purity ethylene is required, when used as a monomer for the production of polyethene as trace amounts of oxygen in the parts per million range can deactivate the polymerization catalyst. Therefore, removal of oxygen without loss of ethylene is a key process step. Overall, the key requirement of the catalyst is to reduce oxygen selectively to water without oxidation or reduction of the ethylene.

**Experimental**

The TAP experiments studied the adsorption and the reaction properties of the main probe molecules (C$_2$H$_4$, O$_2$ and H$_2$) over 2% Ag/γ-Al$_2$O$_3$ catalyst (particle size 150-250 μm), in the 100-200 °C temperature range. Details of the TAP system employed for the study can be found elsewhere (Goguet et al 2006, 2010; Morgan et al., 2010; Shekhtman et al. 2008). The thin zone TAP reactor (TZTR) approach (Shekhtman et al., 1999) was utilized for all the experiments, using silicon carbide (SiC) as the inert packing material. All the gases (H$_2$, O$_2$, ethylene and Ar) used in the experiment had purity of > 99%, and were supplied by BOC. In all experiments, the composition of the pulses from each valve consisted of a 1:1 mixture of reagent to Ar.

**Results**
The preliminary experiments over the one-zone SiC reactor packing indicated that hydrogen or oxygen did not adsorb over this inert material, while, at temperatures \( \leq 100 \) \(^\circ\)C, ethylene showed significant adsorption over SiC.

Figure 2 compares the residence time (first moment) observed for ethylene, oxygen and argon plotted versus the square root of the ratio of molecular weight to temperature. As clearly shown from the magnified scale, argon and oxygen follow the same linear Knudsen dependence given by Equation (1) and reported in Figure 1. However, the residence time for ethylene shows a non-linear dependence with \((\text{Temperature})^{-1}\) with a longer than expected residence time found at low temperatures, which is indicative of adsorption over the SiC. At higher temperatures (>150 \(^\circ\)C), the binding of ethylene to SiC is sufficiently weak for it to follow a linear dependence expected for Knudsen diffusion. Consequently, in order to obtain detailed information about ethylene adsorption over the 2\% Ag/\(\gamma\)-Al\(_2\)O\(_3\) catalysts in the TZTR experiment, the one-zone data recorded over the SiC should be taken into account. Importantly, multi-pulse TAP experiments unravelled that the Ag/\(\gamma\)-Al\(_2\)O\(_3\) catalyst did not convert ethylene to any product up to 200 \(^\circ\)C (see Figure S1 in supplementary information). The pulse response intensity ratio of ethylene to argon was constant, fitting with the one-zone case indicating that ethylene is adsorbed reversibly over the catalyst. This “zero-conversion” case is described by Equations (20) to (24). Using one zone and TZTR pulse response data and Equations (20) to (24), the following results were obtained.

**Influence of the catalyst treatment**

The procedure for the TAP study of ethylene adsorption over the 2\% Ag/\(\gamma\)-Al\(_2\)O\(_3\) catalyst involved packing the reactor with a thin zone of the fresh catalyst (14 mg) followed by evacuation of the reactor and heating to 100 \(^\circ\)C. Then a series of 100 pulse responses of 50/50 ethylene to argon mixture was recorded at 10 \(^\circ\)C intervals over the temperature range 100-200 \(^\circ\)C. Figure 3 shows the subsequent evolution of the ethylene response.

Clearly, with increasing temperature, the experimental curves took a shorter time to reach the baseline. This is indicative of the faster diffusion as well as faster adsorption/desorption processes at high temperature, as would be expected. The
reproducibility analysis showed that once the catalyst was heated above 150 °C and then cooled, the ethylene responses became broader than the corresponding responses observed during the heating of the fresh catalyst sample. As a result of this observation, the difference in behaviour of fresh and thermally treated catalyst was studied to understand the difference in adsorption/desorption characteristics as a function of the pre-treatment. It was also noted that the reduction by hydrogen and oxidation by oxygen produced changes in the adsorption behaviour of the catalyst. Hence, the experiments investigated four different variations of the catalyst, with the varying factor being the way in which the catalyst was treated. Details of these treated catalysts are provided in Table 1.

**Adsorption/desorption properties**

Using equation (23) the first basic kinetic coefficient, $r_1$, was determined from the first moments which were observed in the one-zone and thin-zone TAP experiments. This coefficient is equal to equilibrium adsorption rate constant when only reversible adsorption occurs over the catalyst (Shekhtman et al., 2003):

$$r_1 = \frac{K_a}{K_d}$$

where $K_a$ and $K_d$ are the adsorption and desorption rate constants between ethylene and the catalyst. These are to be distinguished from the adsorption/desorption rate constants over the inert (Equation (2)).

Figures 4 and 5 show the uncorrected and the corrected equilibrium adsorption rate constants, $r_1$, respectively. In each case, the observed $r_1$ values of the four different catalyst treatments are plotted in the logarithmic scale. For both the uncorrected and corrected $r_1$ values the slopes as a function of temperature are similar and the oxidation treatment resulted in the highest observed values of the equilibrium adsorption rate constant. It is clear from these results that the values of uncorrected $r_1$ are significantly greater than those found following correction for the adsorption over the inert material. This is to be expected given that there is a greater contribution of adsorption present in
the uncorrected values as adsorption over the inert material has not been taken into account.

In order to extract the influence of different treatments on the adsorption and desorption rate constants, Equation (24) for the second moments can be used to determine second basic coefficients, \( r_2 \). The coefficients \( r_1 \) and \( r_2 \) make it possible to determine both adsorption and desorption rate constants over the 2\% Ag/\( \gamma \)-Al\(_2\)O\(_3\) catalyst. It is also possible to express the desorption rate constant as a simple ratio [8]:

\[
\left| \frac{r_2}{r_1} \right| = \frac{1}{K_d}
\]

(26)

Thus, the adsorption rate constant can be easily obtained from Equation (25), as both \( r_1 \) and \( K_d \) have been determined. The corrected desorption and adsorption rate constants were calculated from Equations (23) to (26), using the first and second moments observed in the one-zone and thin-zone TAP experiments. Figures 6 and 7 show the uncorrected and the corrected desorption rate constants, respectively. Again, it is evident that the uncorrected results obtained are greater than the values following correction for the adsorption over the inert material.

Figures 8 and 9 show the uncorrected and the corrected adsorption rate constants respectively for each of the pre-treated catalysts as well as the fresh material. In this case a substantial change in the variation with respect to temperature is observed with the corrected values showing the expected trend that the adsorption rate constant decreases with increasing temperature whilst the opposite is true for the uncorrected values. This result emphasises the importance of the correction function given that it is not only the values of adsorption rate constant that are influenced by the adsorption over inert material, but the entire trend. For instance, without the correction function the adsorption rate constant of ethylene appears to increase with temperature, which is not the expected trend. In this case, a conclusion on the elementary steps occurring in the process that is drawn from the uncorrected data would be clearly inaccurate.

From the slopes shown in Figure 7, the activation energies for ethylene desorption were estimated, as reported in Table 2. While the desorption activation energies over
fresh, heated and reduced samples were found to be in the similar range (920-960 J mol\(^{-1}\)), the activation energy over the oxidized catalysts is significantly greater (1067 J mol\(^{-1}\)).

As a different desorption activation energy was observed for the oxidized catalysts, which could be attributed to the different type of ethylene adsorption sites, this was further investigated by a comparison of the diffuse reflectance UV-Vis (DRUV) results for the oxidized and reduced catalysts (Figure 10). It is clear that significant differences exist between the DRUV spectra of the Ag/\(\gamma\)-Al\(_2\)O\(_3\) catalyst oxidised at 200 °C and reduced at 150 °C in either He or H\(_2\). The absorption band in the 200-300 nm range (maximum at 225 nm) under oxidising conditions is attributed to Ag\(^+\) ions. In contrast, under the reducing atmosphere an absorption band forms at 324 nm attributed to silver clusters together with an absorption band at 410 nm attributed to silver particles is observed. This data is consistent with previously reported EXAFS, UV-vis and electron microscopy results which show that even under mild reducing conditions silver is found to aggregate (Breen et al., 2005; Inceesungvorn et al., 2010; Shibata et al., 2003). Therefore, since the activation energy for desorption can be used as an indicator for the structure of the active sites, it is possible that both fresh and reduced catalysts may have a similar structure for the ethylene adsorption sites. This would suggest that the fresh catalyst may be partially reduced, possibly due to reduction under high vacuum in TAP system. Importantly, the similarity between the reduced catalysts is reflected in the corrected values adsorption constant, for example, whereas significant variation was observed for the uncorrected values, demonstrating the importance of being able to take into account the adsorption over the inert material.

In the context of the ability of this catalyst being able to selectively remove oxygen using hydrogen in the presence of ethylene, the corrected TAP data clearly demonstrates that the ethylene adsorption is very low over the catalyst even at low room temperature. This may be compared with oxygen which strongly adsorbs on the catalyst and, therefore, will undergo reaction with hydrogen in preference to the ethylene (see Figure S4 in supplementary information). Such a difference is not obvious from the uncorrected data due to the adsorption over the inert material.

Conclusions
In this paper the issue of adsorption on the inert material used as packing in the TAP micro-reactor is addressed. A theoretical tool which takes into account such adsorption is presented and thus provides a method by which one-zone TAP pulse response experimental data may be interrogated in order to extract detailed kinetic information about the interaction between probe molecules and the catalyst of interest.

The theoretical tool was applied to experimental TAP studies of reversible ethylene adsorption over 2% Ag/γ-Al₂O₃ catalyst. A contribution of ethylene adsorption on the silicon carbide (inert material) was identified below 150 °C. From the results obtained, the adsorption over inert material was found to have a significant impact on the values of adsorption and desorption rate constants. The corrected adsorption and desorption rate constants over the studied catalyst were calculated and then linked to the structure of the catalyst. In addition, from the corrected values it is clear that the high selectivity of the catalyst for the reaction of O₂ with H₂ as opposed to reactions with ethylene can be linked with the low adsorption strength of the ethylene on the silver catalyst.

Acknowledgements
Financial support from EPSRC under the CASTech project, and funding of studentships by the Thai government (BI) and DELNI (KM) are acknowledged.
### Notation

- \( A_r \) cross sectional area of the reactor (m²)
- \( C_I, C_{II} \) concentrations in the first and second inert zones respectively
- \( C_{CS} \) set of catalyst state concentrations (mol/m³)
- \( C_g \) gas concentration (mol/m³)
- \( C_\theta \) surface concentration (mol/m²)
- \( D \) Knudsen diffusivity (cm²/s)
- \( F_{exit} \) dimensionless exit flow
- \( k_a \) adsorption rate constant over inert (cm³ of gas/mol*s)
- \( K_a \) adsorption rate constant over catalyst (cm³ of gas/mol*s)
- \( k_d \) desorption rate constant over inert (cm³ of gas/mol*s)
- \( K_d \) desorption rate constant over catalyst (cm³ of gas/mol*s)
- \( L_{in}, L_{cat} \) length of the inert zone and catalyst zone respectively (m)
- \( L_r \) length of the reactor (m)
- \( L_{TZ} \) length the middle of the thin zone is from reactor inlet
- \( M_n \) moment of \( n^{th} \) order (mole*sⁿ)
- \( M_w \) molecular weight
- \( N_g \) pulse intensity (mol)
- \( r(C_{CS},s) \) Laplace reactivities (1/s)
- \( R_{TZ} \) spatial average reaction rate in the thin zone
- \( r_n \) basic kinetic coefficient of \( n^{th} \) order for \( i^{th} \) probe molecule (sⁿ⁻¹)
- \( s \) Laplace variable
- \( t \) time coordinate (s)
- \( T \) temperature (K)
- \( x \) space coordinate (m)
- \( \tau_{res} \) mean residence time (s)
- \( \tau_{in}, \tau_{cat} \) mean residence time in inert and catalyst zones respectively (s)
- \( \varepsilon, (\varepsilon_{in}, \varepsilon_{cat}) \) bed voidage (in inert and catalyst zone)
Table 1: Details of Catalyst Treatments

<table>
<thead>
<tr>
<th>Catalysts (2% Ag/γ-Al₂O₃)</th>
<th>Treatment process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>-</td>
</tr>
<tr>
<td>Heated</td>
<td>Heated above 150 ºC</td>
</tr>
<tr>
<td>Reduced</td>
<td>Reduced at 150 ºC by H₂/Ar multipulse</td>
</tr>
<tr>
<td>Oxidized</td>
<td>Oxidized at 200 ºC by O₂/Ar multipulse</td>
</tr>
</tbody>
</table>
Table 2: Details of Catalyst Treatments

<table>
<thead>
<tr>
<th>Catalysts (2% Ag/γ-Al₂O₃)</th>
<th>Desorption Activation Energy (J mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>921</td>
</tr>
<tr>
<td>Heated</td>
<td>783</td>
</tr>
<tr>
<td>Reduced</td>
<td>960</td>
</tr>
<tr>
<td>Oxidized</td>
<td>1067</td>
</tr>
</tbody>
</table>
Figure 1: Residence time (first moment, $M_1$) plotted vs. (molecular weight/temperature ($K$))$^{1/2}$ for (Δ) helium, (◊) neon, (●) nitrogen and (■) argon.
Figure 2: Residence time (first moment, $M_1$) plotted vs. (molecular weight/temperature ($K$))$^{1/2}$ for (▲) argon, (■) oxygen, (●) ethylene observed over SiC one-zone packing, with a magnification of argon and oxygen residence times.
Figure 3: Ethene responses over oxidized 2% Ag/γ-Al₂O₃ catalyst. (—) T= 200 °C, (—) T= 190 °C, (—) T= 180 °C, (—) T= 170 °C, (—) T= 160 °C, (—) T= 150 °C, (—) T= 140 °C, (—) T= 130 °C, (—) T= 120 °C, (—) T= 110 °C, (—) T= 100 °C (Broad tails are plotted on magnified scale).
Figure 4: The uncorrected equilibrium adsorption constants, $r_1$, of ethylene observed for (♦) fresh, (■) heated, (▲) oxidized, and (●) reduced catalyst plotted in the logarithmic scale.
Figure 5: The corrected equilibrium adsorption constants, $r_1$, of ethylene observed for (♦) fresh, (■) heated, (▲) oxidized, and (●) reduced catalyst plotted in the logarithmic scale.
Figure 6: The uncorrected desorption rate constants, $K_{d}$, of ethylene observed for (♦) fresh, (■) heated, (▲) oxidized, and (●) reduced catalyst plotted in the logarithmic scale.
Figure 7: The corrected desorption rate constants, $K_d$, of ethylene observed for (♦) fresh, (■) heated, (▲) oxidized, and (●) reduced catalyst plotted in the logarithmic scale.
Figure 8: The uncorrected adsorption rate constants, $K_a$, of ethylene observed for (♦) fresh, (■) heated, (▲) oxidized, and (●) reduced catalyst.
Figure 9: The corrected adsorption rate constants, $K_a$, of ethylene observed for (♦) fresh, (■) heated, (▲) oxidized, and (●) reduced catalyst.
Figure 10: Normalized UV Spectra of Ag/γ-Al$_2$O$_3$ catalyst, oxidized (a) and reduced (b) at different temperatures. 16 °C (black), 30 °C (red), 100 °C (light green), 200 °C (dark blue), 300 °C (light blue), 400 °C (pink) and 500 °C (dark green).
References


