Measuring Adsorption Capacity of Supported Catalysts with a Novel Quasi-Continuous Pulse Chemisorption Method

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An improved pulse-chemisorption technique is presented, which is proven to be independent of the strength of interaction between adsorptive and catalyst material. The methodology is based on the transient mass balance of the adsorptive, allowing for quantitative evaluation of the post-signal obtained from the experiment. Two experimental strategies for determination of the adsorption capacity are introduced, with and without using an internal standard. The methodology is illustratively discussed based on simulation results and verified by chemisorption experiments of hydrogen and carbon dioxide on a supported nickel catalyst. In addition, temperature and dosing effects are examined and benchmarked with volumetric measurements of the adsorption capacity. The proposed mathematical evaluation method of the measured data can be applied directly to experiments performed in standard equipment for pulse-chemisorption or in modified catalyst test rigs to measure adsorption capacity before and after reaction experiments. The technique shows potential for determination of sorption kinetics and combination with operando spectroscopy.

1. Introduction

Sorption experiments for measuring surface area, pore size distribution and metal dispersion, among other physical properties, are highly relevant to characterize supported porous catalysts. Those methods are usually standardized (e.g. ‘BET method’: ISO 9277:2010, volumetric physisorption: ASTM D3663-3, D3908-3, D4222-3, and D4824-13; dynamic physisorption: ASTM D4567-3) and distinguished between physical and chemical adsorption. The latter one is of particular interest for catalyst characterization, as it allows to quantify the active surface area for the desired chemical reaction. Currently, a new method using pulse chemisorption is being developed under the work item WK17123 by ASTM International.[1]

According to the Deutsches Institut für Normung e.V. (engl. German institute for standardization, DIN) chemisorption experiments, for measuring metal dispersions, can be classified as displayed in Figure 1, comprising volumetric, continuous flow and gravimetric techniques.[2] It is usually assumed that volumetric analysis are more sensitive and accurate than flow techniques.[3] Therefore, many examples of volumetric measurements and techniques are available in the literature, which were developed in the last decades.[4] The determination of metal dispersions by flow techniques, instead, is demanding in terms of experimental conduction and data analysis. However, it comes along with the following advantages:[5]

1. The measurements are fast compared to volumetric and gravimetric techniques.
2. Weak bonds between adsorptive and adsorbate, not relevant for typical catalytic reactions, are not detected.
3. A preliminary dead-volume measurement is not necessary.
4. The measurement can be easily tuned for samples with small amounts.

In principle the methodology can be divided into pulse[6] and continuous flow techniques.[7]
While there is no simple and universal method to perform chemisorption experiments, the importance of the topic is evident since chemisorption is one of the elementary steps in reactions catalyzed by solid surfaces. In general, a wide range of experimental methods is described in the scientific literature applying different conditions for pretreatment and execution. Moreover, the setup plays an important role. There are combined techniques described in recent publications, which are not only determining the adsorption capacity. The analysis of adsorption sites and also adsorption strength is performed by temperature-programmed desorption, combined with gravimetric and spectroscopic measurements. So, there is a clear demand for further development of chemisorption techniques.

As an example, the DIN standard gives some advice for the determination of the adsorption capacity of a platinum catalyst by CO pulse chemisorption:

1. The relation between injected adsorptive gas amount and the sample mass, respectively Pt surface area, should be adjusted to have a nearly complete adsorption already during the first pulse.
2. The time interval between the pulses should be constant and long enough that the signal always reaches the baseline.
3. The consecutive pulses should be injected into the system until no increase of the signal area for four consecutive pulses can be detected.

The general advice from the DIN standard provides guidance to perform reproducible pulse-chemisorption experiments. Unfortunately, the pulse flow measurements described in the standard have some pitfalls to be considered.

Probably the most important challenge to be considered is bypass flow in the sample bed, which can turn flow-through in the standard have some pitfalls to be considered. Moreover, the setup plays an important role. Unfortunately, the pulse flow measurements described in the standard have some pitfalls to be considered.

A further challenge is the discrimination between chemically and physically adsorbed gas molecules on the solid surface characterized by the bond strengths. For weakly bound species, adsorption equilibrium needs a sufficiently high partial pressure in the gas phase to achieve a significant coverage on the adsorbance. Meaning that weak adsorption sites on the surface are filled while the pulse with adsorptive passes by, as partial pressure increases during this period. Between the pulses, however, the adsorbed molecules on the weakly binding surface sites are desorbing rather fast again, as equilibrium now favors the species in the gas phase. This behavior can be regarded as a primary advantage of the pulse chemisorption technique since it allows to distinguish between weak and strong adsorption sites, the latter being usually more important for catalytic reactions. However, if the time span between two pulses is too long, stronger bound adsorbates might desorb as well, which impedes the conclusion on the surface taking part in the catalytic reaction. In addition, this behavior will result in a signal not reaching baseline, which conflicts with the advice given above. In a worst-case scenario, the adsorbed species completely desorb between two consecutive pulses, which makes active surface determination unfeasible. Hence, the adsorbed amount strongly depends on a precise control of the pulse frequency, and thus a well-described and reproducible method.

Since chemisorption methods are important tools to determine the active surface area of solid catalysts, several requirements have to be fulfilled in order to allow to link those results with the catalytic performance under reaction conditions. In particular, the following requirements and demands can be formulated for an applicable measurement method, which:

- has to be robust in case of non-ideal breakthrough of the adsorptive,
- has to be reproducible with a simple procedure,
- has to be independent on the chemical nature of the adsorptives and solid surfaces,
- should provide results with little time and labor effort,
- should be performable in a typical catalytic test rig and under reaction conditions (pressure, temperature).

The methodology introduced in the present paper fulfills these requirements to an extent superior to the available standardized procedures. The development of the method is based on theoretical considerations using the dynamic mass balance of the measurement system, which allows to simulate various scenarios with respect to the bond strengths between adsorptive and solid surface. Using the expected signals derived from simulation experiments, a correct procedure for conducting the experiments and for evaluating the raw data is deduced. The proposed methodology is then applied to some typical examples studied by respective physical experiments. The emphasis was put on alumina supported nickel catalysts analyzed with the adsorptives H₂ and CO₂ for experimental demonstration and validation. Finally, a comparison between the proposed technique and a standard volumetric measurement is provided, which allows the evaluation against a well-known reference. Due to the particularities of the proposed technique, it is designated as ‘quasi-continuous pulse chemisorption method’.

2. Method development

2.1. Experimental implementation

The sample material is usually pretreated to obtain a defined surface condition prior to an experimental characterization. Depending on the material class, drying to remove adsorbed water species and subsequent reduction of metal oxides to their metallic counterparts are typical pretreatment steps. The respective procedures and conditions applied, however, depend on the specific sample material used. Since the reduction step is usually carried out in a reducing atmosphere (e.g. hydrogen-containing) at elevated temperatures, transformation of the
solid particles over time may occur, with sintering of metal nanoparticles or support as well as developing metal-support interactions having great importance for the obtained characterization results. Following the reduction step, the sample is flushed with inert gas at pretreatment temperature or above to remove adsorbed compounds from the sample and to obtain a clean surface for examination of the specific adsorption capacity. Evacuation of the sample to support the removal of adsorbed species is beneficial but not performed in this study, because it is usually not possible in typical catalyst test rigs. Finally, the sample is cooled down under inert gas flow to the designated adsorption temperature.

A typical experimental setup is depicted in Figure 2. Pulses are injected via a sample loop, which allows loading, following the black lines, with pulse gas and injection, following the red lines, with carrier gas. The pulse chemisorption measurement is started after achieving a constant inert gas flow through the sample cell (carrier gas) and a stable flow of adsorptive containing gas (pulse gas) through the sample loop. During injection of the stagnant molar amount in the sample loop the total molar flow rate is unaffected.

Prior to injection of the first pulse from the sample loop into the carrier gas, the measurement signal from the analytics is stabilized. The dosage of adsorptive containing gas is performed according to the following scheme (Figure 3). In the first step, the sample loop is filled with adsorptive. The duration of the filling step depends on the gas flow rate and volume of the sample loop. It is recommended to check the necessary time for complete exchange. Before injection, the sample loop has to be equilibrated regarding temperature and pressure to ensure a constant amount of substance of the adsorptive in each pulse, which is done by stopping the flow through the sample loop for a few seconds. The static pressure is usually also attained within this time. Afterward, the injection of adsorptive gas into the system is performed by flushing the sample loop with inert carrier gas. Here, the back-mixing of the adsorptive during the injection period has to be considered as a possible source of measurement errors. Depending on the diameter of the sample loop, laminar flow can be assumed in most cases accompanied by entrance effects. After ensuring complete injection the sample loop is switched back to the loading position. Pulse dosage is repeated until no change in the maxima is detectible and a uniform signal shape is obtained for five subsequent pulses. Note that the mentioned intervals are exemplary, and a scheme with 60 s for an injection cycle is used. It thus becomes clear that the term ‘quasi-continuous’ refers to the character of the process, which in contrast to the classical pulse chemisorption does not only inject several pulses consecutively, but a series of pulses with a constant frequency. The adjustable frequency allows measurements with separated individual pulses at low frequencies, as well as measurements with overlapping pulses at high frequencies. As a boundary case at infinite frequency a continuous operation is even reached, which is not relevant to the aims of the measurements, though. It is important to repeat all steps with the same time duration and minimal deviations in injection frequency. As a rule of thumb, a deviation in duration for each step of below 200 ms is recommended.

2.2. Signal processing

Typically, the effluent concentration of the adsorptive is analyzed after leaving the measurement cell and a characteristic signal for the pulse chemisorption experiment described above is obtained as shown in Figure 4. The signal corresponds to the
concentration of the adsorptive in the gas phase measured by a thermal conductivity detector (TCD) or a mass spectrometer (MS), both allowing for sufficiently high sampling frequencies. The obtained course of the signal can be divided into three sections, with distinct characteristics. In the first unsaturated section (index u,1), the peak area is increasing with each consecutive pulse reaching saturation during the last pulse within this section. The following saturated section (index s) is characterized by a constant height, shape and area of each consecutive peak, which indicates that the injected amount of adsorptive is identical to the amount leaving the system. Since the duration of each individual pulse is identical, as stated above, the duration of this section is always an integer multiple of the time chosen for one single injection cycle. Finally, during the second unsaturated section (index u,2) weakly bound species desorb from the surface, leading to a more or less pronounced tailing of the signal until the baseline is reached. The integrated signals of both unsaturated sections (light grey) and the saturated section (grey) are indicated in Figure 4 along with the start $t_{\text{start}}$ and end time $t_{\text{end}}$ of the measurement.

### 2.3. Calculation of adsorbed amount

The calculation of the accumulated amount of the adsorbate is derived via a material balance, which is formulated for the molar amount of adsorbate species $i$, based on the following assumptions:

1. The sample volume can be described as an isothermal open system.
2. The obtained signal is proportional to the adsorptive molar fraction in the gas phase.
3. The volumetric flow rate of the adsorptive/carrier gas mixture is constant throughout the experiment, hence the molar flow of adsorptive leaving the sample cell is directly proportional to the signal.
4. For a saturated catalyst surface, each consecutive pulse is invariant of the chosen phase within the period. Therefore, two successive pulses have the same shape.

The respective general transient material balance of an open system [Eq. (1)] relates the accumulation of material by adsorption ($\dot{n}_{\text{ad}}$) to the inlet ($\dot{n}_{\text{in}}$) and outlet ($\dot{n}_{\text{out}}$) flow rates of compound $i$. Integration over time gives the adsorbed amount of substance of the adsorbate A [Eq. (2)].

\[
\frac{dn_{\text{ad}}}{dt} = \dot{n}_{\text{in}} - \dot{n}_{\text{out}} 
\]

(1)

\[
n_{\text{ad}} = n_{\text{in}} - n_{\text{out}}
\]

(2)

In general, the dosed amount can also be derived from integrating the molar flow rate of $A$ over time [Eq. (3)], which is either the exact molar flow rate or an averaged value. The presented method is based on the pulse technique, where the adsorptive is injected with a certain frequency $f$ into the system. Here $f$ is the reciprocal value of the time interval between two consecutive pulses. For the dosing, an average flow rate of $A$ [Eq. (4)] can be used since the amount of substance $A$ in the sample loop is completely injected into the system with the injection frequency $f$. For a given time interval, the cumulative dosed amount $n_{\text{in}}$ of adsorptive can be obtained by Equation (5) with the number of injections $N$. Therefore, the amount of substance $A$ in the sample loop (index: SL) is calculated from the respective temperature, pressure and volume based on the ideal gas law and multiplied with the mole fraction of the adsorptive $x_A$ in the sample loop before injection. The measurement effort to calculate the injected amount of substance reduces to temperature and pressure, assuming that all other values are constant ($R$, $x_A$), specified in datasheets ($V_{\text{SL}}$) or known ($N$).

\[
\dot{n}_{\text{in}} = \int \dot{n}_{\text{in}}(t) \, dt = \int \dot{\hat{n}}_{\text{in}} \, dt 
\]

(3)

\[
\dot{\hat{n}}_{\text{in}} = f x_A \frac{p_{\text{SL}} V_{\text{SL}}}{R T_{\text{SL}}}
\]

(4)

\[
n_{\text{ad}} = N x_A \frac{p_{\text{SL}} V_{\text{SL}}}{R T_{\text{SL}}}
\]

(5)

One of the main benefits of the presented method is that the partial pressure of the adsorptive in the carrier gas stream during injection can be varied. According to Equation (6), the dosed amount of $A$ can be varied by changing the pulse frequency. With a constant carrier gas flow rate $\dot{\hat{n}}_{\text{CG}}$, different mean partial pressures or mole fractions of $A$ can thus be adjusted (Equation (6), see also section 2.1). These considerations give rise to measure the adsorption capacity by varying the pulse frequency in flow experiments since the adsorptive partial pressure in the gas phase can be adjusted thereby. Thus
far, only volumetric methods are used to investigate adsorption isotherms by direct variation of the partial pressure.

\[ \hat{x}_{A,\text{in}} = \hat{n}_{A,\text{in}} / n_{CG} = f(x_k \frac{p_{CG}}{p_{SL}} T_{CG} V_{SL} / T_{SL} V_{CG} \]  

(6)

According to the proportionality between the obtained signal and the adsorptive concentration, the outlet molar flow rate can be derived by Equation (7) with the calibration factor \( F \) and the carrier gas flow rate \( \hat{n}_{CG} \). The total molar amount of adsorptive leaving the system can be calculated by integrating the transient signal \( S \) [Eq. (8)].

\[ \hat{n}_{A,\text{out}}(t) = x_{A,\text{in}}(t) \hat{n}_{CG} = F S(t) \hat{n}_{CG} \]  

(7)

\[ \hat{n}_{A,\text{out}} = \int_{t_0}^{t_f} \hat{n}_{A,\text{out}}(t) \, dt = F \hat{n}_{CG} \int_{t_0}^{t_f} S(t) \, dt \]  

(8)

In the saturated region, the signal is periodic by definition (see Sec. 2.2). Thus \( S(t) \) is identical for each individual pulse \( j \) and a limit cycle is reached. Consequently, the amount of adsorbate adsorbed during one period is identical, and the effective accumulation is zero, as expressed by Equation (9). This allows to rewrite Equations (5) and (8) leading to Equations (10) and (11) for each pulse \( j \). Then, the combination of which results in Equation (12). Importantly, Equation (12) allows for in-situ determination of the calibration factor \( F \), which depends strongly on the detector sensitivity and may vary between the different detectors. This approach is not limited to one single substance in the gas phase if the applied detector allows to distinguish between different compounds (e.g. MS).

\[ n_{h,\text{inj}} = n_{A,\text{out}} \]  

(9)

\[ n_{h,\text{inj}} = x_k \frac{p_{CG}}{p_{SL}} V_{SL} / T_{SL} \]  

(10)

\[ n_{h,\text{adj}} = F \hat{n}_{CG} \int_{t_0}^{t_f} S_j(t) \, dt \]  

(11)

\[ x_k \frac{p_{CG}}{p_{SL}} V_{SL} / T_{SL} = F \hat{n}_{CG} \int_{t_0}^{t_f} S_j(t) \, dt \]  

(12)

The value \( \alpha_u \) is thus used to determine the adsorbed fraction of adsorptive injected and can be derived from the signal at the outlet of the sample cell. Therefore, the overall mass balance [Eq. (2)] is expressed with discrete injections [Eq. (17)]. The accumulated adsorbate \( n_{A,\text{adj}} \) is equal to the difference between injected and leaving amount of adsorptive. The injected amount of adsorptive \( n_{A,\text{inj}} \) is calculated from a known amount of adsorptive in the sample loop \( n_{A,SL} \) and a known number of total pulses \( N_{\text{inj}} \). The amount of adsorptive leaving the sample cell \( n_{A,\text{out}} \) is separated into the saturated and unsaturated region [Eq. (15) and (16)]. The former can be calculated by the number of saturated pulses \( N_s \) and the adsorptive amount in the sample loop, while the unsaturated region is affected by adsorption expressed by the adsorption ratio \( \alpha_u \). After rearranging (with \( N_{\text{inj}} = N_s + N_u \)) Equation (18) is derived, which allows the determination of the adsorbed amount by the adsorption ratio in the unsaturated region, only. Importantly, a calibration factor between the content of adsorptive in the gas stream and the signal is required, for quantification of \( \alpha_u \). Therefore, Equation (18) is expanded to cover all injections \( N_{\text{inj}} \) which allows to express the total fraction of accumulated adsorptive related to the injected amount \( \alpha_{\text{tot}} \). Note that \( \alpha_{\text{tot}} \) can be expressed by the measured signals, as will be shown in the following sections (see description of methods M I and M II below).

\[ n_{A,\text{adj}} = N_s n_{A,SL} - N_u n_{A,SL} - (1 - \alpha_u) N_{\text{inj}} n_{A,SL} \]  

(17)

\[ n_{A,\text{adj}} = N_{\text{inj}} n_{A,SL} \alpha_u = N_{\text{inj}} n_{A,SL} \alpha_{\text{tot}} \]  

(18)

The material balance is either calculated with an internal standard (M II) and/or with a basic method (M I). Both methods can be found implemented in Excel and Python in the supporting information.
2.4. Method (M I): Basic Method

The basic method can be applied to any system where solely the adsorptive concentration in the exit gas is analyzed. Here, the saturated pulses can be used as in-situ single-point calibration. For the calculation of the total adsorption ratio, the saturated pulses are needed to scale the adsorbed amount [Eq. (19)], where the denominator is the expected total area with adsorption [Eq. (15)], while the numerator is the measured area with adsorption. Therefore, the signal is divided into three parts (two unsaturated and one saturated, see Sec. 2.2). After rearranging and combination of Equations (18) and (19), the adsorbed amount can be calculated by Equation (20).

\[
\alpha_{\text{tot}} = 1 - \frac{\Delta t_{u,1} S_{u,1} + \Delta t_{s} S_{s} + \Delta t_{u,2} S_{u,2}}{N_{\text{tot}}} \quad (19)
\]

\[
n_{h,\text{ad}} = N_{\text{tot}} n_{A,\text{SL}} \left( 1 - \frac{N_{i}}{N_{\text{tot}}} \frac{\left( \Delta t_{u,1} S_{u,1} + \Delta t_{s} S_{s} + \Delta t_{u,2} S_{u,2} \right)}{\Delta t_{s} S_{s}} \right) \quad (20)
\]

2.5. Method (M II): Internal Standard

In cases where the analytics allow to distinguish between different gas species (e.g. MS), the usage of an internal standard is beneficial. The corresponding evaluation method is based on referring the obtained signals for the adsorptive to those of the internal standard. The advantage is that already small changes of the volumetric flow rate due to adsorption are fully compensated by referring to the internal standard. Equation (21) provides the definition for the respective calibration factor \( F \) as a ratio of the cumulative molar amount of adsorptive A and internal standard IS leaving the system during the saturated region. In contrast, the ratio of the cumulative molar amounts of both compounds leaving the system during the whole experiment, meaning in the saturated and unsaturated region together, is expressed in Equation (22). This equation displays a measured ratio of adsorptive to internal standard \( z_{\text{meas}} \), which is comparable to the numerator in Equation (19), while \( F \) is the denominator. After the combination of Equations (21) and (22) with Equation (18) and rearrangement, the adsorbed amount of substance can be derived by Equation (23). This equation is structurally identical to Equation (20), though the adsorption ratio is calculated with reference to the internal standard.

\[
F = \frac{n_{h,\text{ad},A}}{n_{h,\text{ad},IS}} = \frac{\Delta t_{s} S_{s,A}}{\Delta t_{s} S_{s,IS}} \quad (21)
\]

\[
z_{\text{meas}} = \frac{n_{h,\text{tot}}}{n_{h,\text{tot},IS}} = \frac{\Delta t_{u,1} S_{u,1,A} + \Delta t_{s} S_{s,A} + \Delta t_{u,2} S_{u,2,A}}{\Delta t_{u,1} S_{u,1,IS} + \Delta t_{s} S_{s,IS} + \Delta t_{u,2} S_{u,2,IS}} \quad (22)
\]

\[
n_{h,\text{ad}} = N_{\text{tot}} n_{A,\text{SL}} \alpha_{\text{tot}} = N_{\text{tot}} n_{A,\text{SL}} \left( 1 - \frac{z_{\text{meas}}}{F} \right) \quad (23)
\]

2.6. Signal processing

To determine the necessary parameters for the two different calculation methods, signal separation into the three distinct regions, according to Figure 4, is necessary. Therefore, the obtained minima in the signal are used to identify each individual pulse. Subsequently, the pulses are compared by signal shape \( S(t) \) in order to observe a recurrent shape, which is characteristic for the saturated region. This can be done graphically, for instance, plotting the signal two times with a time shift of the injection interval. Pulses attributed to the saturated region are those framed by two identical pulses within certain error margins. In other words, the first and last pulse defining the range of the saturated region are those, which are identical and frame the largest number of pulses in between, which are all identical as well. Thus, the saturated region starts at the preceding signal minimum, defined as \( t_{\text{lim},1} \). Since an integer number of pulses is dosed, the end of the saturated pulses can be defined by the obtained number of saturated pulses \( N \), and the time duration for each pulse [Eq. (24)].

\[
t_{\text{lim},2} = t_{\text{lim},1} + N \frac{1}{T} \quad (24)
\]

The two unsaturated regions are preceding and succeeding the saturated one and are limited by the start \( t_{\text{start}} \) and end \( t_{\text{end}} \) of the experiment, respectively. The start of the experiment can be defined according to the number of pulses prior to reaching the saturated region and their duration. Since tailing occurs in many cases following the last pulse, the end of the experiment should be set in order to provide sufficient time reaching baseline signal. In most cases, five times the duration of one pulse fulfills this requirement. It is noteworthy that in contrast to TPD experiments (e.g. \([12,13]\)), where desorption peaks appear during temperature increase that can be associated with the binding strength of the adsorbates, the signal tailing in the second unsaturated region for pulse-chemisorption experiments is caused by desorption taking place at constant temperature.

The analysis of the desorption behavior, however, is very important for the quantitative interpretation of the adsorption capacity of the sample, as it contains information on weakly adsorbed species although the signal-to-noise ratio makes the equilibrium challenging. Due to the transient concentration changes of the adsorptive in the gas phase during each pulse, the equilibrium with the species adsorbed at the solid surface is affected. Consequently, the measured signal represents a superposition of adsorption and desorption depending on surface coverage and gas-phase concentration at each point in time. In order to consider the desorption behavior in the analysis, we include the tailing in the analysis as well and distinguish the rate of desorption as follows:

1. The signal at \( t_{\text{lim}} \) and at \( t_{\text{end}} \) is the same, providing that \( t_{\text{end}} \) is reached according to the residence time distribution of the system: no desorption of the adsorptive is observable.
2. The adsorptive is constantly desorbing with a low molar flux over several multiples of the hydrodynamic residence time, leading to a constant signal and with higher values at \( t_{\text{end}} \) compared to \( t_{\text{start}} \); slight desorption is observable.

3. The adsorptive is desorbing with a decreasing molar flux over several multiples of the hydrodynamic residence time; strong desorption is observable.

It should be noted that technical challenges, such as the pumping efficiency of mass spectrometers, also have an influence on the signal in particular during tailing. The results presented in this work, though, are not affected by those errors, since a sealing gas purge was used.

In the first case, the interactions between the adsorbate and the solid surface are strong. Thus, the adsorptive is easily adsorbed unless the solid surface is fully covered and desorption is not occurring. Consequently, the measured signal requires no further adjustment, since desorption is not affecting the measured signal.

The second case is more complicated since the unsaturated regions are affected by constantly desorbing adsorbate. In other words, the signal decrease is small within the time period considered for tailing analysis. The low desorption rate increases the signal \( S(t) \) by a constant offset, which can be determined from the tailing at the end of the experiment (\( S(t = t_{\text{end}}) \)). Since the coverage of the adsorbate \( \theta \) is not influenced, Equation (25) can be assumed to be still valid (BODENSTEIN’s quasi steady state assumption). Therefore, the mean signal can be calculated from the second limit \( t_{\text{lim2}} \) to the end \( t_{\text{end}} \). This value is corrected by the desorption signal via subtraction of the tailing after the last pulse until the end \( t_{\text{end}} \) (linear offset adjustment, see Equation (26)). Here \( t_{\text{end}} \) is the expected time when effective desorption starts. If pulses are included in the second unsaturated region, signal adjustment for desorption is necessary after the last pulse.

\[
\frac{d \theta}{dt} = 0 \tag{25}
\]

\[
\tilde{S}_{\text{lim2}} = \frac{1}{(t_{\text{end}} - t_{\text{lim2}})} \int_{t_{\text{lim2}}}^{t_{\text{end}}} S(t) dt - S(t_{\text{lim2}})(t_{\text{end}} - t) \tag{26}
\]

For the third case, the interaction of adsorptive and adsorbent is weak, resulting in a strong desorption after a decrease in partial pressure of the adsorptive in the gas phase. Due to the high desorption rate, the adsorbate coverage is continuously decreasing, which explains the decrease in the signal after the last pulse according to a first-order desorption behavior. In this case, the first and second derivatives of the signal help to analyze the desorption behavior. If the signal is non-zero, there will be some desorption, as stated above in the second case. If the first derivative is non-zero, there is a change in the molar flux from the surface, which can be further analyzed by the second derivative. The second derivative provides the opportunity to separate different desorption processes through the change of the molar flux. Due to the high number of possibilities, we do not want to propose a certain procedure at this point. However, it should be pointed out that a fitting of the desorption kinetics is possible according to Equation (28) since the measurable molar flow of the adsorptive is proportional to the desorption rate, which can be fitted by a first-order desorption kinetics.

\[
S'(t) = \frac{d^2 S_{\text{lim2}}(t)}{dt^2} \tag{27}
\]

\[
h_{\text{A, out}}(t) \sim r_{\text{A, des}}(t) = k_{\text{A, des}}(T) n_{\text{A, out}}(t) \tag{28}
\]

2.7. Simulation

The processing methodology is illustrated by two simulative examples with a different extent of desorption (Figure 5). The respective governing equations of the simulation model are

**Figure 5.** Comparison of two simulated pulse-chemisorption measurements with different desorption rates \( (r_{\text{des}}) \); grey area represents the saturated region for reference; \( t_{\text{end}} \) is the end of signal evaluation.
shown in the supporting information. For illustration, the rate of a first-order desorption kinetics is varied. This corresponds to a change in the activation energy of the desorption reaction. The resulting signals for a simulated pulse-chemisorption for both examples are comparable with distinct differences regarding the tailing and amplitude. While the signal reaches the baseline after 320 s for the low desorption rate (case 1), a continuously decreasing signal can be observed for the example with the higher desorption rate (case 2). Therefore, no desorption is noted for the former, while strong desorption is found for the latter case, according to the case classification in Sec. 2.6. Additionally, the amplitude in the saturated region (grey area) is smaller for the case 2, exhibiting smaller maximum and higher minimum values. This can be explained as follows: The high desorption rate corresponds to a low activation energy, which means that the adsorptive is less strongly bound to the solid surface. This causes desorption during the phases with lean adsorptive concentrations and thus increasing signals. Consequently, the surface coverage is reduced and the adsorption capacity is increased for the following phase rich in adsorptive, which is responsible for the opposing observation of reduced signal maxima.

The presented evaluation methodology is used to determine the adsorption capacity with method MI for both simulated cases (Table 1) using different approaches for analysis of the tailing. Case 1 and 2b are evaluated by applying the appropriate tailing treatment, according to the respective desorption regime identified from the simulation results, and show good agreement with the expected adsorption capacity of 6 μmol. In contrast, case 2a exhibits a significant deviation, since the tailing was analyzed assuming no desorption, even though case 2 was identified to be governed by strong desorption. As already mentioned, discrimination between the slight and strong desorption regimes is challenging, especially using real experimental data. Thus, slight desorption was assumed to be appropriate for case 2, even though simulation results indicate the strong desorption regime. The estimation error of less than 1.5%, however, appears to be negligible.

A significant degree of freedom in quantitative analysis of the signal is the ending of the measurement t_end, which is defined by the operator. As can be seen in Figure 5 for case 2, a signal is still apparent after more than 360 s. In real cases, the deviation from the baseline might not be that obvious, though. Since the molar amount desorbing beyond t_end is not considered in the evaluation, the position of t_end has a high impact on the calculated adsorption capacity. Figure 6 illustrates the impact of the position of t_end on the calculated adsorption capacities for case 2. The values in Table 1 are calculated at the position of t_end indicated in Figure 6. The error decreases for smaller time durations, while it increases for longer times. For very small time durations, the influence of residence time distribution can be seen by a change in the gradient (between 20 and 30 s in Figure 6). For very long time durations, the calculated amount will be significantly affected by noise, since the signal-to-noise ratio approaches small values.

It is also apparent, that the point t_end has a different sensitivity for each case. A low desorption rate (solid black line) shows just a small decrease over time. So, the position of t_end has a small impact on the calculated adsorption capacity. For the other two cases, the position will have a significantly higher influence on the calculated amount of substance, although an adjustment is already applied (dashed black line). It should be ensured that the sensitivity of t_end has a small influence. This can be shown by calculating the rate of desorption for the next minute from t_end (see Equation (29)). A transparent measure of the sensitivity can be given by the ratio of desorbed amount and the calculated amount adsorbed at t_end (see Equation (30)), which corresponds to a change in coverage per minute. The simulated results in Figure 6 have a change in coverage of 0.08% min⁻¹ for low r dés and 4.22% min⁻¹ and 1.18% min⁻¹ for high r dés.

\[
\Delta \theta = \frac{n_{A,ad}(t_{end}) - n_{A,ad}(t_{end} + 60 \text{ s})}{n_{A,ad}(t_{end})}
\]  

(29)

\[
\frac{n_{A,ad}}{\Delta t} = \frac{n_{A,ad}(t_{end}) - n_{A,ad}(t_{end} + 60 \text{ s})}{60 \text{ s}}
\]  

(30)

Thus, the proper choice of the time interval for evaluation of the adsorbed amount remains challenging and might require
detailed analysis and additional pre-experiments in some cases. Nevertheless, reliability can be indicated by the sensitivity of the values obtained.

**Experimental Part**

**Catalysts**

The experimental study is performed with an 11 wt.-% Ni/Al\(_2\)O\(_3\) catalyst prepared via incipient wetness impregnation of γ-Al\(_2\)O\(_3\) with nickel nitrate.\(^{[14]}\) Therefore, the 160–250 μm sieve fraction of the support, the nickel salt and additional water are heated to 80 °C, mixed after melting of the nickel salt and subsequently dried under moving air in a furnace at 80 °C. Finally, the dried catalyst is calcined in a muffle furnace under N\(_2\) atmosphere for 12 h at 400 °C after temperature increase with 5 K min\(^{-1}\). Prior to chemisorption experiments, the Ni/Al\(_2\)O\(_3\) catalyst is reduced at 450 °C for 12 h in a flow of 10.1% H\(_2\)/Ar (heating rate from ambient temperature 3 K min\(^{-1}\)).

**Experimental Setup**

The flow chemisorption measurements are performed in a BelCat-M (Bel-Japan Inc.) catalyst-testing unit, equipped with a calibrated sample loop with a volume of 1.0125 cm\(^3\), which corresponds to a gas amount of ca. 40 μmol at ambient temperature and pressure. The device has two gas lines, one for the carrier gas (Ar, He) and one for the pulse gas, respectively. The injection of the sample loop is achieved manually with a 6/2-way valve.

The catalyst sample is fixed in a concentric quartz glass reactor (see Figure 7) with an inner diameter of 5 mm by quartz wool. The gas flow is fed annularly for pre-heating before entering the reactor below the sample with upwards flow. The volumetric flow rate of 30 mL\(_{STP}\) min\(^{-1}\) for all gases is adjusted by a needle valve and measured with a piston-based flow meter (DCL-ML, Bios International Corporation). The reactor is operated at ambient pressure. The sample is placed in a furnace, which can be heated up to 1000 °C with a maximum heating rate of 30 K min\(^{-1}\). The temperature control is realized with a thermocouple (Typ K, NiCr–Ni) shielded by a quartz glass capillary. A fraction of the exhaust gas is analyzed with a quadrupole MS (GAM 200, InProcess Instruments), which is coupled to the exhaust by a quartz capillary with an inner diameter of 50 μm and heated to 200 °C to prevent condensation of water. Gas molecules are ionized by a Wolfram filament, which is powered with 70 V. The signal is amplified with a secondary electron multiplier at 1200 V, resulting in an amplification factor of 14 for He (4 amu). The ionization chamber operates at a pressure of 3 · 10\(^{-5}\) mbar. The MS is equipped with a sealing gas purge, which stabilizes pump efficiency and hinders back-diffusion into the measurement chamber. The remaining exhaust gas is passed over a molecular sieve to remove water before flowing through a thermal conductivity detector (TCD).

The concentration of the gases is measured with the mass spectrometer using a multiple ion detection. For the H\(_2\) chemisorption, the m/q-ratios at 2 (H\(_2\)), 4 (He), 17 (H\(_2\)O), 32 (O\(_2\)), 40 (Ar) are measured, while for the CO\(_2\) adsorption the m/q-ratios of 4 (He), 17 (H\(_2\)O), 28 (CO, CO\(_2\)), 32 (O\(_2\)), 40 (Ar), 44 (CO\(_2\)) are used. Each ratio is measured for 20 ms before the next higher ratio is approached. The overall measurement time is 0.5 s for a complete cycle.

**Experimental Procedure**

For dynamic pulse chemisorption measurements, ca. 80 mg of the catalyst are placed in the sample tube and reduced in-situ with H\(_2\) as described above. Afterward, the reduced catalyst is flushed for 2 h with an inert gas to remove adsorbed hydrogen and water at a...
temperature of 460 °C and ambient pressure. Subsequently, the chemisorption experiments are conducted according to the method described above after natural cooling to 50 °C under inert gas flow. Preliminary tests reveal that 20 pulses or more should be applied in order to obtain reliable data. Furthermore, significant drift in the analytics was ruled out during the time of measurement for each experiment.

Volumetric chemisorption measurements are performed with a 3Flex device (Micromeritics). The reduction procedure for the catalysts corresponds to that for the dynamic chemisorption experiments, while heating and cooling steps are performed under vacuum. Evaluation of the volumetric chemisorption isotherms is performed with the back-extrapolation of the linear part of the isotherm to zero pressure (see section 3.1.2.2.2 in Singh et al.\cite{15}). Further information on the volumetric adsorption measurements can be found in the SI, including data for another catalyst system.\cite{16}

**Exemplary Results**

In the following, selected examples are presented in order to demonstrate the broad applicability of the pulse chemisorption methodology. Therefore, the evaluation method (according to Sec. 2.4 and 2.5) is varied and comparatively discussed. All raw data from this section are accessible and can be used to reproduce the results obtained here (see SI).

**Small desorption rate constant**

Figure 8 shows the MS signal for a 11 wt.-% Ni/Al\textsubscript{2}O\textsubscript{3} catalyst using H\textsubscript{2} as adsorptive. The pulse gas contains 10.1 vol.-% H\textsubscript{2} in Ar, which offers the latter to be used as an internal standard in this experiment. Each injection took 60 s, which sums up to 20 min for 20 pulses followed by 30 min tailing, in order to analyze this phase in detail. As expected, the internal standard shows all 20 pulses applied to the system with equally shaped peaks. The comparison between internal standard and adsorptive reveals that H\textsubscript{2} is completely adsorbed in the first pulse, with increasing peak heights for the subsequent pulses. The adsorptive signal approaches the periodic time-invariant limit cycle at 800 s with the 11\textsuperscript{th} pulse. After the last pulse, both gases approach the baseline rather fast. While the internal standard follows the residence time distribution, due to the absence of interaction with the solid surface, the adsorptive is affected by the superposition of desorption and residence time distribution. However, the deviation between both signals is relatively small. Thus, according to the classification in Sec. 2.6 the interaction between adsorptive and active surface is strong, which consequently implies a low desorption rate constant.

The resulting adsorption capacity as a function of the tailing duration, obtained applying both evaluation methodologies M I and M II, can be seen as inset in Figure 8. The calculated adsorption capacity is also shown for tailing adjustment for both methods (labeled with adj.). The accumulated amount of substance is asymptotically approaching constant values at about 2500 s, respectively. Even though the asymptotic value for the results appears to be identical, the unadjusted determination gives flat profiles, while the results with adjusted tailing are noisy with increasing intensity. This is because the standard method uses integral values, which already dampens the measurement noise, while the noisy signal at t\textsubscript{res} affects the whole adjustment of the tailing. The amplification of noise can be explained by the increasing noise-to-signal ratio with increasing tailing duration. This drawback of tailing adjustment should be considered in data interpretation and can be minimized by averaging.

**High desorption rate constant**

The same experiment was conducted using CO\textsubscript{2} as adsorptive, He as internal standard and Ar as carrier gas. The measured signals and the calculated adsorption capacities are depicted in Figure 9. At first sight, the signal for the CO\textsubscript{2} measurement seems to be comparable to H\textsubscript{2}, though two main differences can be observed: The first pulse is not completely adsorbed, thus a minor peak can be observed at 250 s and the tailing is still observable beyond 1500 s. The adsorption capacity was evaluated without and with linear adjustment of the tailing at 2500 s and assuming case one and case two according to classification in Sec. 2.6. Apparently, the assumptions of both cases are not fully met for this measurement. It is noteworthy that the obtained signal can be considered constant after 2500 s with adjustment of the tailing, because case two seems to become valid after this time. The inset shows the respective results of adsorption capacities. A continuous decrease in capacity without approaching an asymptotic value is observed.

![Figure 8](image.png)

**Figure 8.** Measured signal for internal standard (grey, Ar) and adsorptive (black, H\textsubscript{2}) adsorption on Ni/Al\textsubscript{2}O\textsubscript{3} in He as carrier gas; inset: calculated adsorption capacity over tailing duration with basic method (M I) and using internal standard (M II) using tailing adjustment (adj.) or using standard processing.
for both methods, if no tailing adjustment is included in the evaluation. Considering the tailing in data analysis by linear adjustment still exhibits a continuous decrease in adsorption capacity despite some scattering, which indicates the necessity of a more complex tailing analysis for more reliable adsorption capacity determination. Compared to the typical practice of pulse-chemisorption data evaluation, though a capacity of ca. $3\mu$mol can be derived in the present example with significant reliability. This value is much lower than the capacity derived from $H_2$ adsorption, which can be explained by different adsorption stoichiometry and support contribution. However, these explanations cannot be verified on the basis of the current data.

Figure 10 depicts the molar flow rates desorbing from the catalyst in the tailing phase calculated by methods M I and M II. While the desorption rate for $H_2$ is close to zero after 2250 s, a significant amount of $CO_2$ is still leaving the catalyst. The $CO_2$ desorption can be distinguished in two regions, irrespective of the evaluation method applied. In the first phase, weakly bound $CO_2$ is desorbing leading to a rather strong gradient in desorption rate until ca. 2000 s. In the following phase, the gradient is decreasing since the weakly bound species are already fully desorbed and stronger bound ones are desorbing slowly. Consequently, according to the classification in section 2.6, strong desorption is observable for pulse-chemisorption with $CO_2$ on Ni/Al$_2$O$_3$. Even though linear adjustment is not suitable for those cases, it is applied here as an approximate for the more complex case of strong desorption. The interpretation of Figure 9 and Figure 10 together consequently exhibits that the applicability of the simplified adjustment procedure can be verified based on the results derived from the evaluation methods. Moreover, the sensitivity for both measurements with $t_{end}$ at 2500 s shows reliable values for both measurements. Adsorption of $H_2$ shows a change in coverage (see Eq. 30) of below 0.05 % min$^{-1}$ for all calculations. For $CO_2$ the change in coverage is above 1 % min$^{-1}$ for the standard calculation and below 0.1 % min$^{-1}$ for calculation with tailing adjustment, assuming case two according to classification in Sec. 2.6. A more complex procedure can be systematically applied at a later stage, depending on the requirements for accuracy of the adsorption capacity. This might also include the assumption of adsorption sites with different adsorption properties (e.g. stoichiometry and enthalpy).

**Dosing frequency and reproducibility**

Reproducibility was checked together with a variation in injection frequency for the Ni/Al$_2$O$_3$ catalyst. The measurement was conducted with the pulse gas $H_2/Ar$ in a carrier gas stream of He and thus for case one according to classification in Sec. 2.6, as proven in the previous section. Consecutively, three measurements were performed with a 60 s injection period, followed by two measurements with 30 s and 120 s, each. Between the experiments, desorption of adsorbed $H_2$ was ensured by treatment at 460 °C for 2 h. The number of pulses was kept constant at 20 for each experiment. Results were analyzed using methods M I and M II and shown in Table 2 as the deviation from the target value.
Table 2. Reproducibility and influence of dosing frequency on adsorption capacity derived via M I (basic method) and M II (using internal standard), values for measurements 1 to 7 are deviation from target value for adsorption capacity given in bottom line.

| Measurement | Injection period [s] | Deviation\[VI\] [μmol] |
|-------------|----------------------|------------------------|
|             |                      | via M I                |
|             |                      | via M II               |
| 1           | 60                   | –0.09                  |
| 2           | 60                   | –0.08                  |
| 3           | 60                   | –0.13                  |
| 4           | 30                   | –1.23                  |
| 5           | 30                   | 0.06                   |
| 6           | 120                  | –0.01                  |
| 7           | 120                  | 0.10                   |
| target value/μmol |                  | 5.04                  |

\[VI\] Deviation in adsorption capacity from target value.

Table 3. Comparison of adsorption capacity of Ni/Al₂O₃ catalyst for H₂ and CO₂ at different adsorption temperatures, two results from flow measurements to show reproducibility.

| Adsorptive | T [°C] | Volumetric [μmol g⁻¹] | Flow [μmol g⁻¹] |
|------------|--------|------------------------|-----------------|
| H₂         | 50     | 114                    | 114             |
|            | 200    | 106                    | 93              |
| CO₂        | 50     | 184                    | 84              |
|            | 200    | 82                     | 11              |

Except for measurement 4, all deviations are within 10% limits, which corresponds to the typical accuracy for chemisorption (≤ 10–15% for H₂ and CO adsorption). Moreover, the deviation between both methods is far below 10%. Furthermore, the scattering in deviation for different dosing frequencies is smaller than for reproducibility. In other words, the adsorption capacity can be obtained with different dosing frequencies within the desired accuracy bounds for pulse-chemisorption. Even though the evaluation method applied affects the deviation towards the target value, the results are within the accuracy region and thus not significantly depending on the method. The similarity of the results obtained by M I and M II also validate the assumption of a constant flow rate, which is mandatory for M I but not required for M II, due to compensation by an internal standard.

Interestingly, the variation in the pulse frequency corresponds to a different mean partial pressure of the adsorptive, as pointed out in Sec. 2.3. In particular, the averaged partial pressure over time decreases with increasing injection period durations. Consequently, the results reported in Table 2 indicate that no increase of the adsorbed amount with increasing averaged partial pressure is detected, since the deviations from the target value show no significant trend. This may be due to the following reasons. Either, the variation in the partial pressure in our experiments is too small to achieve a new point of the adsorption isotherm or full adsorption, i.e. a saturated monolayer is already achieved. In addition to that, it has to be considered that the deviation between the experiments might be more pronounced than the increase of the adsorbed amount at a higher partial pressure of the adsorptive.

Comparison to volumetric measurements

The comparison between the dynamic pulse chemisorption and the volumetric chemisorption is used to provide proof of the ability to determine the monolayer coverage with the proposed methodology. Therefore, the impact of adsorptive and temperature on the chemisorption measurement results was studied for Ni/Al₂O₃ catalysts. H₂ was chosen as strongly adsorbed compound and CO₂ for the weakly bound case. The temperature for chemisorption experiments was set to 50 and 200 °C in order to extend the study to higher temperatures relevant for thermo-catalytic reactions, such as the dynamic methanation of CO₂. Furthermore, the adsorption strength might be more relevant at higher temperatures, where weakly bound species are probably not present during the experiment.

The results for the obtained adsorption capacity via method M II are shown in Table 3. For both adsorptives, the capacity is decreasing with increasing temperature in volumetric measurements, which is in line with the decrease in the equilibrium constant for the exothermic adsorption process. For H₂, the obtained adsorbed amounts are comparable for both techniques at each temperature, with a deviation of below 10% and reproducible for the flow technique. However, the differences between flow and volumetric method are more pronounced for higher temperatures, probably due to the lesser strength of adsorption. This explanation is supported by the significant deviation between flow and volumetric measurement for CO₂, which was identified to be a weakly adsorbing molecule (see Sec. ‘High desorption rate constant’). Taking into account the significant CO₂ adsorption on the Al₂O₃ support material as a reason, the flow method thus appears to be selective to quantify strongly bound species rather than the overall adsorption capacity. In other words, adsorptive molecules desorbing at strong binding sites are irreversibly bound and thus not desorbing during lean periods in the gas phase, while weakly bound molecules are desorbing during those periods releasing a free sorption site for the subsequent pulse. Consequently, the volumetric and flow technique provide complementary information on the sorption behavior.

Recent findings by Ewald and Hinrichsen gave additional insight into adsorption of CO₂ on Ni/Al₂O₃. For volumetric adsorption measurements, it was observed that CO₂ dissociates upon adsorption, while this is not the case for the pulse chemisorption technique. During static adsorption, all adsorption sites on the Ni crystals and on the alumina are filled, whereas the pulse method only leads to an occupancy of the strong adsorption sites. Whether the strong binding sites are on the alumina or the Ni particles cannot be accessed with this method. This explains the lower values observed for CO₂ with the proposed flow method. However, the investigation of the interactions between supported catalysts and CO₂ remains a current issue. For strongly binding adsorptives, the measured adsorption capacities by volumetric and flow techniques are in good agreement, which sets the validated basis to distinguish between strongly and weakly bound species by quantitative comparison of results obtained with both methods.

3. Conclusions

Quasi-continuous pulse chemisorption was introduced as a novel flow technique for measuring adsorption capacities. The method was developed by mathematical modelling and numerical simulation of transient mass balances and experimentally verified by various examples with emphasis on Ni/Al₂O₃ catalysts and the adsorptives H₂ and CO₂. The method provides fast experimental procedures and high reliability of the obtained results comparable to volumetric measurements. Preparatory calibration of the analytics is helpful but not required, since a single point calibration can be extracted from the measurement signal itself. Slightly adsorbing gases or weak interactions between adsorbent and solid surface, as well as
non-ideal breakthrough behavior will not affect the accuracy, due to the robustness of the proposed analysis. Furthermore, the method can in principle be applied to typical flow setups with little effort, i.e. adding a sample loop, in order to derive sorption data in-situ prior to or following reaction experiments. Finally, the evaluation method is not limited to ambient pressure, though this was used for experimental validation in the present contribution, as long as reliable pulse-chemisorption data are provided by the particular experiment under elevated pressure.

The presented method provides interesting opportunities for further investigation in the field of adsorption measurements. In particular, multicomponent adsorption and thus the interaction of adsorptives can be measured with capable analytics, e.g. MS, if chemical reactions can be excluded during the experiment. Those experiments are not possible with current volumetric techniques, but provide detailed insight into the interaction of different adsorptives relevant to combined adsorption or reaction experiments. Therefore, sorption specific operando-spectroscopy, such as diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), operando Raman or UV-Vis, are powerful tools.[7,8] However, in order to receive the maximum information, a reliable mass balance is mandatory, as shown in the present paper.

### Nomenclature

| Indices | Description |
|---------|-------------|
| A | adsorbate gas |
| ad | adsorbed |
| cal | calibration |
| CG | carrier gas |
| in | inlet |
| meas | measured value |
| out | outlet |
| SL | sample loop |
| s | saturated |
| u | unsaturated |

| Variables and parameters | Description |
|--------------------------|-------------|
| $S$ | signal |
| $\bar{S}$ | average signal |
| $T$ | temperature |
| $t$ | time |
| $t_{\text{end}}$ | time, end of measurement |
| $t_{\text{start}}$ | time, start of measurement |
| $\Delta t$ | time interval |
| $V$ | volume |
| $x$ | mole fraction |
| $z$ | ratio of signals |
| $\alpha$ | adsorption ratio |
| $\theta$ | coverage |
| $f$ | pulse frequency |
| $F$ | calibration factor |
| $k_{\text{des}}$ | rate constant of desorption |
| $N$ | number of injections |
| $n$ | amount of substance |
| $n$ | molar flow rate |
| $\bar{n}$ | average molar flow rate |
| $p$ | pressure |
| $r_{\text{des}}$ | rate of desorption |
| $R$ | ideal gas constant |

### Acknowledgements

Bjarne Kreitz gratefully acknowledges the fruitful discussion with Prof. Dieter Bathen from the Institute of Thermal Process Engineering of the University Duisburg-Essen on adsorption. The authors gratefully acknowledge the provision of PURALOX® support material by Sasol Germany GmbH. Open access funding enabled and organized by Projekt DEAL.

### Conflict of Interest

The authors declare no conflict of interest.

### Keywords
adsorption · chemisorption · measurement · pulse · transient

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Manuscript received: February 17, 2020
Revised manuscript received: May 18, 2020
Version of record online: July 10, 2020