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Determination of Extinction Coefficients for Describing Gas Adsorption on Heterogeneous Catalysts Using In-Situ DRIFT Spectroscopy

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Abstract: Diffuse reflection infrared Fourier transform (DRIFT) spectra have been quantitatively evaluated to determine unknown extinction coefficients as well as the number of active surface centers and the amount of adsorbed species. Sulfated zirconia with *n*-butane as probe gas was used as model system. For quantitative evaluation of *n*-butane adsorption at 323 K, the sulfate band S=O at 1400 cm^{-1} was chosen. During adsorption, this band is red-shifted to lower wavenumbers accompanied by a structural change of the band indicating isomerization reaction. By analyzing difference spectra and determining the areas of the selected band, the extinction coefficients as well as the number of active centers and the amount of chemisorbed *n*-butane were calculated. The quantitative evaluation results in a mean internal decadic extinction coefficient of 60 cm^{-1} μmol^{-1}, an average amount of *n*-butane adsorbed to the sulfated zirconia of about 4 µmol, and a number of active centers of around 21 µmol/g. These results correspond very well with values from the literature obtained by microcalorimetry. Thus, this method is suggested to be transferred also to unknown systems of interest.

Keywords: DRIFT spectroscopy; extinction coefficients; zirconia; *n*-butane; adsorption

1. Introduction

The calculation of extinction coefficients via measured IR spectra is discussed in the literature in many ways, and there are a number of different approaches to determine quantitative data from the measured spectra. What all of these approaches have in common is that the measurements were performed using transmission IR-spectroscopy. The method, which is recognized as reference source for the determination of extinction coefficients from infrared spectra, was developed by Emeis in 1993 [1]. He investigated the adsorption of pyridine on Si/Al-based catalysts and defined an integrated molar extinction coefficient (IMEC) characteristic for one special absorption band with the assumption that the IMEC does not depend on the catalyst or the strength of the acid site. The integrated absorbance of one band was plotted against the pyridine concentration. The IMEC can then be calculated from the slope of the linear regression. The calculated IMEC values were 1.67 cm/µmol for the Brønsted acid site at 1545 cm^{-1} and 2.22 cm/µmol for the Lewis acid site at 1455 cm^{-1}.

As in the work of Emeis, most of the studies to determine extinction coefficients from IR spectra are carried out via transmission infrared spectroscopy. Morterra et al. [2] studied the adsorption of methanol on silica and discussed the use of molar absorption coefficients in heterogeneous systems. Their results show that absorption coefficients cannot easily be transferred from one system to another due to different specific surface areas, sample thicknesses, and scattering properties. However, absorption coefficients could be compared for systems/samples with similar properties and measuring conditions.

Jentoft et al. [3] described that extinction coefficients may not be readily transferable from one adsorbent to another. They investigated the adsorption of *n*-butane and neopentane on sulfated zirconia using transmission infrared spectroscopy and determined the integrated molar absorption coefficients for the adsorbate vibrations. The work revealed difficulties and limitations to measure accurately IR absorption coefficients because of scattering effects of the method and strong dependencies of the coefficients on particle size and morphology. In conclusion, there are limitations with respect to the quantitative analysis of transmission IR spectra for fine powders. Molar absorption coefficients can be determined assuming that the system conforms to Lambert-Beer behavior [4]. For those determinations, the measurement of integrated band areas and number of adsorbed moles (simultaneously using volumetric gas dosing or something else) is required. To relate the signal intensity to the number of adsorption sites, it is necessary to determine the absorption coefficients. For those calculations it is assumed, that the coverage has no influence on the absorption coefficients and that there are no intermolecular interactions. In summary, the calculation of molar absorption or extinction coefficients from transmission infrared spectra works under certain assumptions, but cannot be easily transferred to other measurement methods.

Diffuse reflection infrared Fourier transform (DRIFT) spectroscopy is a non-invasive method that offers the advantages of in-situ investigations of powdered catalyst samples (in contrast to transmission measurements), and is therefore often used for the qualitative investigation of the interaction of catalyst surfaces and adsorbents [5]. The main drawback of this method is the difficulty of quantitative measurements, the reproducibility of measurements (the diffusion coefficients varies with each measurement), and the temperature gradient between the upper edge and the bottom of the crucible [6]. Thus, further quantitative evaluation of such spectra is affected by the measuring principle of diffuse reflection itself. Nevertheless, spectra obtained by DRIFTS measurements can be evaluated quantitatively in addition to their qualitative information content.

The main goal of this work was to evaluate opportunities for an easy way to quantitatively evaluate DRIFT spectra. These quantitative data should then serve as a starting point for further adsorption experiments of various probe gases and lead to a deeper understanding of the interaction of catalysts and adsorption gases with respect to a microkinetic model of alkane conversion and the influence of acid or base sites of zirconia.

The quantitative evaluation of DRIFT spectra is not very common in the literature. Meunier et al., investigated in 2007 the water-gas shift reaction on Au-based catalysts using quantitative DRIFT spectroscopy [7,8]. They concluded that with careful experimentation and a calibration of the measured data for each catalyst, it is possible to perform fully quantitative operando DRIFTS. A comparison between diffuse reflectance and diffuse transmittance spectroscopy was done by Boroumand [9]. They found that inhomogeneities in the surface of the sample powder are equally important and nonnegligible.

Therefore, it can be concluded that special attention must be paid to the preparation of the samples to ensure reproducibility and that the extinction coefficients obtained are specific to one special measurement system.

The most common theoretical model for converting a diffuse reflection spectrum into a spectrum comparable to a transmission or extinction spectrum was introduced by Kubelka and Munk already in 1931 and was developed in an effort to determine the thickness required for a covering paint coat. They developed the following equation (with R denoting the reflectance of an infinitely thick layer):

$$\frac{S}{K} = \frac{(1 - R_\infty)^2}{2 \cdot R_\infty} \quad (1)$$

While the scattering module S for homogeneous samples with the same packing density is regarded as constant for many applications, the absorption factor K is directly proportional to the concentration c or the molar decadic extinction coefficient ε. Using DRIFTS experiments and a known weakly absorbing reference spectrum (for example potassium bromide), the term $(1-R_\infty)^2/(2 \cdot R_\infty)$ can

be measured. Thus, a quantitative evaluation of the spectrum obtained from the diffuse reflection with regard to the existing proportionality to the concentration and the molar decadic extinction coefficient is possible. In order for the Kubelka-Munk transformation to lead to usable results in quantitative evaluation, the sample must be homogeneous and similar in its packing density, have an isotropic scattering (particle size < wavelength of light used), and have a sufficiently large layer thickness (several millimeters).

As a model system and an example for the quantitative evaluation of DRIFT spectra and the calculation of molar exctinction coefficients, the adsorption of *n*-butane on sulfated zirconia was chosen. This system has already been widely studied due to the good catalytic properties of sulfated zirconia for the skeletal isomerization of small alkanes at low temperatures. Examples of this are the investigations of Wrabetz [10], Li [11], Breitkopf [12], and Gonzáles [13], which were carried out with microcalorimetry. In these investigations, the surface of the activated sulfated zirconia was characterized and the number of active sites and sorption heats were determined. Therefore, this results in a good data situation to compare and validate the values determined in this study with quantitative DRIFT spectroscopy.

In the literature, absorption coefficients of zirconia have mostly been determined to quantify the number of adsorption sites on the solid acid surfaces (Lewis and Brønsted sites) through the adsorption of basic probe molecules such as pyridine. By means of transmission IR measurements, absorption coefficients of 1.00–2.08 cm/µmol (Lewis sites) and 0.64–1.66 cm/µmol (Brønsted sites) were obtained. In addition, various studies showed that changes in the preparation method have effects on the specific absorption coefficients [4].

Values for absorption coefficients for sulfated zirconia determined using DRIFT spectroscopy are not found in the present literature due to the difficulties described before. This paper presents an approach to determine extinction coefficients for the adsorption of gases on sulfated zirconia aware of the difficulties and with the awareness that the values determined are only specific to a special measuring system. Nevertheless, the described method and the calculated specific extinction coefficients are a good prerequisite for the investigation of unknown systems and useful as a starting point for further quantitative investigations.

2. Results and Discussion

2.1. Adsorption of n-Butane on Sulfated Zirconia

Absorption spectra before and after adsorption of *n*-butane on sulfated zirconia (SZ) at 308 K are shown in Figure 1. Before purging, the gas phase bands of *n*-butane at 2950 and 1466 cm^{-1} are clearly visible. The absorption maxima of the gas phase bands of *n*-butane increase with increasing number of *n*-butane injections via the loop according to the higher concentration. The change in the characteristic sulfate band at 1400 cm^{-1} was used to describe the SZ and *n*-butane interaction as well as to determine the extinction coefficients. The band at 1400 cm^{-1} can be assigned to the stretching vibration of the S=O bond, which is associated in the literature with a disulfate structure on the surface of the catalyst [12,14]. It has a double-band structure with a maximum at 1400 cm^{-1} and a shoulder at 1375 cm^{-1} with lower intensity. During the adsorption of *n*-butane, the S=O band is red-shifted to lower wavenumbers. The double-band structure initially remains, but the intensity decreases. Unfolding the double band resulted in a shift of 10 cm^{-1} for the maximum at 1400 cm^{-1} and about 30 cm^{-1} for the shoulder. From the 5th loop onwards, only the absorption maximum increases and there is no further shift of the sulfate band. This indicates a saturation of the proposed active centers. Furthermore, an isosbestic point at 1395 cm^{-1} can be observed, which points to a probable transformation of S=O bound in S–O–H with bounded *n*-butane. A red-shift of bands in the hydroxyl region about 3750 cm^{-1} supports these indications. However, the structure of the S=O band itself changes indicating the isomerization reaction. After 15 min of purging with nitrogen to remove physisorbed *n*-butane, the sulfate band is still located at 1390 cm^{-1}, which clearly shows the adsorption of *n*-butane on the sulfated zirconia.

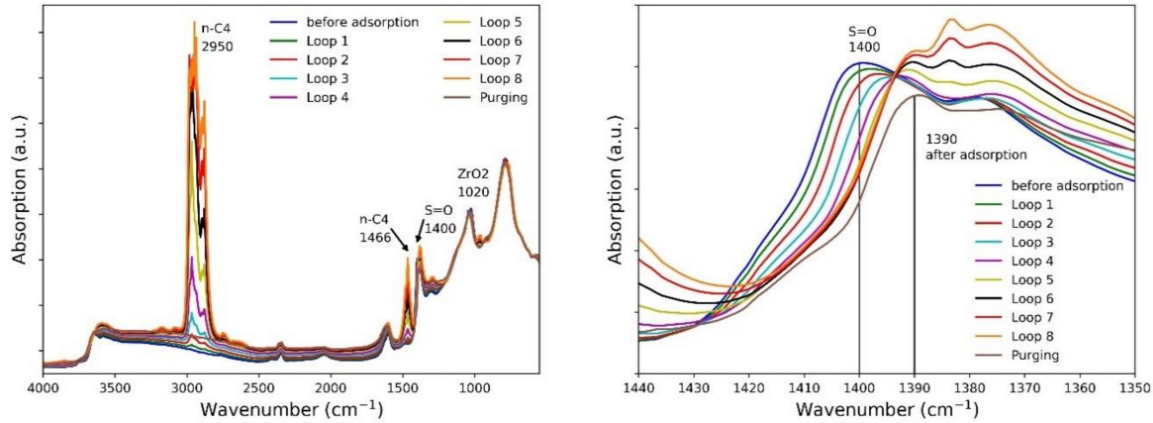


Figure 1. DRIFT spectra for adsorption of *n*-butane on sulfated zirconia at T = 308 K.

The change of the double-band structure, the meaning of the isosbestic point for structure changes and the amount of the shifts will be investigated in more detail in subsequent works with the help of spectral deconvolution and theoretical calculations (Density Functional Theory, DFT) as the quantitative evaluation of the spectra itself is not affected by the shift.

2.2. Determination of Extinction Coefficients

The characteristic S=O band at 1400 cm^{-1} was chosen for detailed analysis. The shift of the S=O band resulting from the adsorption of the probe molecules and the analysis of difference spectra (subtraction of the spectra recorded during the adsorption from the spectrum recorded before the adsorption) allows the determination of the signal areas caused by the shifted S=O band. The signal areas are calculated by integrating the selected S=O band in the same wavenumber range for all measurements. In accordance with Lambert-Beer's law, the product of the molar decadic extinction coefficient ε and the optical sample thickness d from the slope in the resulting straight lines can be determined from the application of the injected probe molecule concentration c or the associated amount of substance (x-axis) relative to the determined signal area A (y-axis), which is proportional to the adsorbed particle amount.

$$A = d \cdot \varepsilon \cdot c \tag{2}$$

Since the optical sample thickness d remains constant for the same measuring instrument, an internal reference value for the extinction coefficient is determined from the slope of the straight line (see also Figure 2). This also results in an adapted unit for the internal extinction coefficients (namely cm^{-1} µmol^{-1}) in contrast to the absorption coefficients given in the literature, which include the surface of the pressed disk or the optical thickness of the sample (unit cm µmol^{-1}). This means that the extinction coefficients determined in this study do not correspond to the common extinction coefficients (given in the literature) and cannot be easily compared to the absorption coefficients given in the literature determined by transmission IR measurements. Nevertheless, the determined values are consistent for one measuring instrument and transferable to other sample systems.

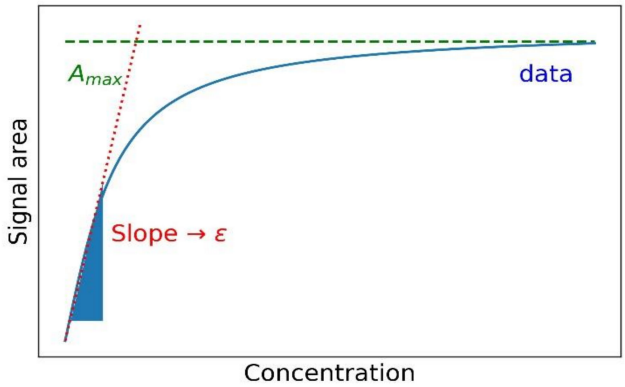


Figure 2. Determination of extinction coefficient. (The green dotted line represents the maximum detected signal area, the red dotted line is the linear slope of the data curve).

If the unit [cm^{-1}] is assigned to the signal area, then the ratio of the maximum detected signal area A_{max} (occurs to the saturation of the active centers, coverage ratio $X = 1$) and the internal extinction coefficient ε determined from the straight line slope with the unit [cm^{-1} μmol^{-1}] can be used to determine the amount of substance $n_{adsorbed}$ of the total gas molecules adsorbed on the catalyst in [µmol] according to Equation (3).

$$n_{adsorbed} = \frac{A_{max}}{\varepsilon} \tag{3}$$

The number of active centers on the catalyst surface in [µmol/g] can then be extracted by relating the amount of adsorbed material to the mass of catalyst used for the respective experiment. The calculated active centers can then be used for comparison with literature values and thus represent a possibility to check the reliability of the method.

To calculate the extinction coefficients of the example *n*-butane/SZ, first all spectra are baseline corrected and the difference spectra between the zero spectrum before adsorption and the respective adsorption spectrum (for each loop) are calculated (see Figure 3). The signal areas for each difference spectrum are then calculated in the same wavenumber range from 1340 to 1420 cm^{-1} and normalized to the amplitudes of the respective experiment. After normalizing the signal areas obtained in this way to the amplitudes of the respective experiment, the uniformity of the adsorption processes can be shown with the adsorption isotherm according to Figure 4. Therefore, the adsorption was similar in all experiments. From the fifth loop on at the latest, the amplitudes of the respective experiments and thus the saturation of the active centers are reached. Overall, it is stated that the adsorption experiments were similar and thus comparable. This further indicates a good reproducibility of the experiments.

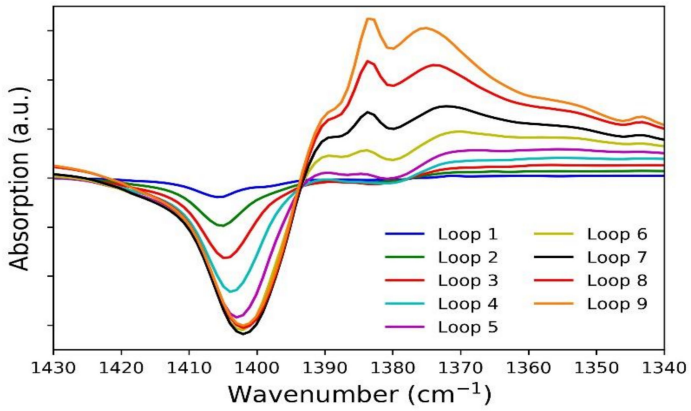


Figure 3. Difference spectra for adsorption *n*-butane on sulfated zirconia (SZ) at $T = 308$ K. ("Loop 1" corresponds to the difference spectrum between Loop 1 and the spectrum before adsorption and so on.).

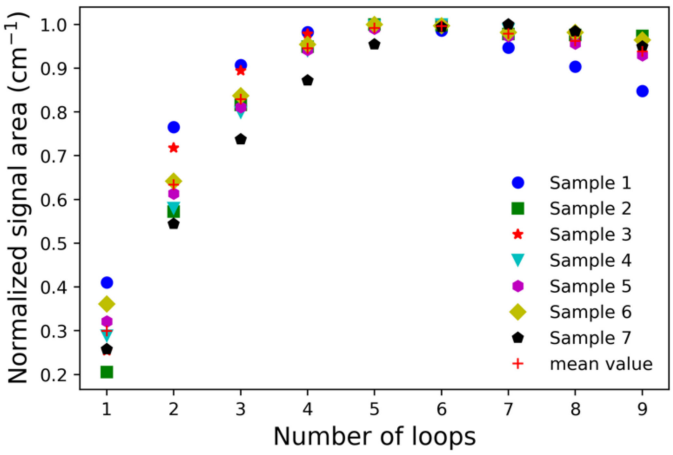


Figure 4. Adsorption isotherm of *n*-butane on SZ at T = 308 K for all experiments.

Both the calculation of the extinction coefficients and the determination of the adsorbed *n*-butane quantities are shown exemplarily for the results of one experiment. All other experiments were evaluated in an analogous manner, the results are summarized in Table 1.

Table 1. Evaluation results of the adsorption of *n*-butane on SZ.

Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**Ø**
A_{max} [cm^{-1}]	33.09	893.76	590.81	56.61	89.19	67.4	81.03	-
ε [cm^{-1} µmol^{-1}]	8.177	204.68	142.7	13.003	21.037	15.715	18.245	**60.5**
$n_{adsorbed}$ [µmol]	4.05	4.37	4.14	4.35	4.24	4.29	4.44	**4.27**
Number of active centers [µmol g^{-1}]	20.25	21.85	20.7	21.75	21.2	21.45	22.2	**21.35**

The determined signal areas are plotted against the number of loops, i.e., the *n*-butane concentration (Figure 5). Knowing that the doses with *n*-butane are in the µmol range, an internal molar decadic extinction coefficient is determined with the help of linear regression as described above. All relevant variables for the entire adsorption evaluation are summarized in Table 1. A mean decadic extinction coefficient of 60 cm^{-1} µmol^{-1} was determined by this procedure. For all experiments, only the ratio of signal area amplitude and extinction coefficient is approximately constant (see Table 1). However, the absolute values of the signal area amplitude and the extinction coefficient are subject to a large fluctuation. The determination of an unambiguous extinction coefficient is therefore only regarded as a rough approximation due to the large deviations.

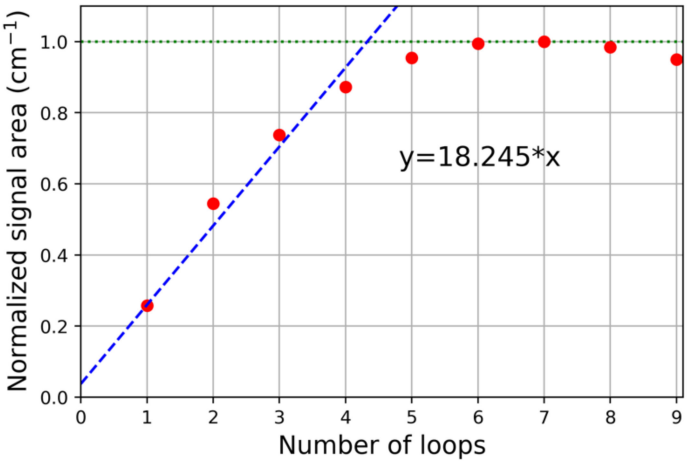


Figure 5. Adsorption isotherm of *n*-butane on SZ at T = 308 K.

The quantitative evaluation results in an average amount of *n*-butane adsorbed on SZ of about 4 µmol. If 200 mg SZ material is used, this corresponds to a number of active centers of around 20 µmol/g.

The values determined for the number of active centers in this study correspond very well with the values determined in the literature using microcalorimetry to investigate the adsorption of *n*-butane on sulfated zirconia [10,11], which determined values of 20 µmol/g for sulfated zirconia (5 wt% sulfate) and 60 µmol/g for SZ with 9 wt% sulfate. Gonzales [13] also determined by microcalorimetry a number of active centers of 35 µmol/g for the adsorption of *n*-butane on SZ. The comparison of the values determined here with those determined by microcalorimetry shows that the proposed method based on DRIFT spectroscopy is quite suitable for the quantitative investigation of sorption reactions, if certain conditions are given. The extinction coefficients in particular cannot simply be transferred to another measuring system, but are nevertheless very helpful in the investigation of other unknown, interesting systems.

3. Materials and Methods

3.1. Catalyst Preparation

The zirconia was produced by precipitation with ammonia solution from the respective nitrates. First, a defined amount of the nitrate is dissolved in distilled water and stirred until the salt is completely dissolved. The pH value of the solution is then adjusted to 8.4 by adding drops of a 25% ammonia solution while stirring continuously. Aqueous zirconium hydroxide precipitates as a white gel-like precipitate. The reaction mixture is stirred, filtered, and the filter cake is washed three times with distilled water. The filter residue is then dried at 393 K for 24 h.

For sulfation, the dried precursor material is first ground, suspended, and mixed with aqueous $(NH_4)_2SO_4$. This suspension is concentrated to dryness while stirring and then dried in air at 373 K for 24 h. The nominal sulfate content was 5 wt%. Elemental analysis was used to determine a mean sulfate content of 3.4 wt% for all samples.

For removal of water and other impurities contained, the samples were calcined in synthetic air flow (0.2 L/min) at 873 K for 3 h one day before the experiments.

3.2. Diffuse Reflection Infrared Fourier Transform Spectroscopy (DRIFTS)

DRIFTS measurements were done using a Praying Mantis Accessory (Harrick Scientific Products, Pleasantville, New York, NY, USA) with the High Temperature Reaction Chamber (HCV, Harrick Scientific Products, Pleasantville, New York, NY, USA) and a home-made injection loop in a Bruker Vertex 80 v FTIR spectrometer (Bruker Optik GmbH, Leipzig, Germany). Spectra of ground KBr powder were used as background for the experimental measurements. The samples (mass 200 mg, not diluted with KBr) were ground for homogeneity and then activated in the reaction chamber at 673 K for 1 h with 0.1 L/min nitrogen purging. The adsorption of *n*-butane was done at 308 K using a home-made injection loop until saturation of the sample was visible in the measured spectra (8–10 times). The injection loop was filled 5 min with *n*-butane. The adsorption time was 10 min per injection loop with one recorded spectrum per minute. After complete adsorption, the sample was purged for 25 min with 0.1 L/min to eliminate physiosorbed and non-adsorbed *n*-butane. The experiments were repeated ten times to check the reproducibility.

The spectral resolution used was 2 cm^{-1} and the number of averaged scans was 32. The wavenumber range was from 8000 to 500 cm^{-1}. The analysis of the spectra was done with OPUS software.

4. Conclusions

Using the adsorption of *n*-butane on sulfated zirconia as an example, a method was shown to determine extinction coefficients as well as the adsorbed amount of gas and the number of active sites under reaction conditions by DRIFT spectroscopy. In this study, an internal mean extinction

coefficient of 60 cm^{-1} μmol^{-1} for the adsorption of *n*-butane was calculated. Approximately 4 µmol of *n*-butane were adsorbed on the SZ surface and the number of active sites was 21 µmol g^{-1} on average. These values correspond very well with values from the literature, where the number of active sites for the *n*-butane/SZ system were determined by microcalorimetry. The calculated adsorption isotherms are consistent for a certain number of experiments provided that the measured spectra are normalized for the particular experiment. Great care must also be taken in sample preparation and a constant measurement routine in order to obtain comparable results. Under the given conditions, DRIFT spectroscopy is then suitable to be used for the quantitative investigation of sorption reactions instead of transmission measurements and to overcome the disadvantages of transmission measurements.

With the help of the results of this study, the corresponding desorption reactions will be quantitatively investigated in further studies and desorption heats will be calculated. The results can thus be transferred to other interesting systems and offer good starting points and conditions for further investigations. With the help of theoretical calculations, the spectral changes during the sorption reactions will be further investigated in order to gain even deeper insights into structure-activity relationships of sulfated zirconia.

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