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Light alkane interactions on transition metal oxides like zirconia using a combined frequency response and DRIFTS study

Rebecca Grün, * Maja Glorius and Cornelia Breitkopf

The frequency response (FR) technique is a powerful method for investigating mass transport in porous materials. Although it is well established in the field of microporous solids, FR is rarely used in the context of mesopores. This study aims to contribute to further exploring this particular field. To this end, sulfated zirconia with ethane, propane, iso-butane, *n*-butane, and neopentane as adsorptives was selected. While DRIFT spectroscopy is used to investigate the interaction of alkanes with sulfate groups of zirconia, the frequency response method is applied to draw conclusions about coupled diffusion and adsorption processes. For this purpose, the model of Reyes *et al.* for FR of gases in mesopores (*J. Phys. Chem. B*, 1997, **101**, 614–622) is applied in comparison to the simplified case of effective diffusion. It is shown that diffusion coefficients are obtained in the range of the Knudsen regime, while adsorption is quantified in good agreement with the adsorption capacity derived from the adsorption isotherms. Effective diffusion coefficients are evaluated as a result of the interaction of adsorption and diffusion. This research not only aims to apply the model of Reyes *et al.* to a homemade volume swing FR method for the first time, but also to further pave the way for the systematic investigation of mesoporous materials using FR and DRIFTS.

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Introduction

In view of growing demands for environmental compatibility as well as energy savings and climate protection, there is an increasing need for more environmentally friendly catalysts for the isomerization of light alkanes and the subsequent production of olefins by oxidative dehydrogenation. This method is seen as an alternative to established processes such as steam cracking, fluid catalytic cracking or catalytic dehydrogenation.[1,2] The aim is to replace highly acidic catalysts – such as those based on aluminum chloride, which are corrosive and harmful to the environment – with more sustainable solutions. Promising catalysts for isomerization include transition metals in form of sulfated zirconium dioxide (SZ) compounds, which are highly catalytically active at low temperatures and are also environmentally friendly.[2,3] In order to optimize such high-performance solids for industrial processes, detailed knowledge of the mass transfer of reactants is essential. Such insights not only influence the large-scale process design, but also help to clarify reaction mechanisms as well as the deactivation behavior of the catalyst.

Since sorption and transport are highly intercorrelated, the detailed analysis of mass transfer processes of gases in porous materials is a challenging task. It requires transient measurements, which can shed light on key aspects of the behavior of gases inside the pore system. To this end, frequency response (FR) can be applied as transient investigation method.[4,5]

In short, the thermodynamic equilibrium between gas and solid is disturbed within FR by periodically changing the volume of the closed system marginally. In the present case, the method is classified as volume swing frequency response (VSFR). The application of a rectangular perturbation function to a solid/gas system generates a characteristic response that depends on the frequency of the respective perturbation.[6,7] The detection of response peaks in FR spectra provides information on the time constants of the corresponding mass transfer processes. Ultimately, the FR method extracts adsorption and mass transfer quantities for the gas under investigation in the porous solid. The specific FR method used here has already been applied to microporous materials.[8,9]

So far, mesoporous materials have generally been studied only scarcely using the FR method.[10–15] The aim is therefore to broaden this technique now to mesoporous materials in order to demonstrate the great potential of FR, which is rather simple in terms of instrumentation, but can be extended considerably

Chair of Thermodynamics, Technische Universität Dresden, 01069 Dresden, Germany

in terms of modeling. Overall, the detailed analysis of mesopores using VSFR technique represents a large blind spot in the pertinent literature, although mesoporous solids, such as silica or aluminosilica in addition to zirconia, are well-established catalysts and support materials for heterogeneous catalysis. Within a widely recognized study, Reyes *et al.*[11] used mesoporous silica spheres as a packed bed with nitrogen, xenon, a nitrogen/xenon mixture, and iso-butane as adsorptives for frequency response studies. Varying the bed height was found to have no influence on the FR intensity, so the bed effect was considered negligible. In addition to the widely-used frequency response models according to Yasuda,[4,16] which consider diffusion or adsorption separately each, the authors propose a theoretical model that couples diffusion and adsorption in mesopores. FR results (spectra) with an identical or similar shape typical for diffusion (pure diffusion spectra) can thus be analyzed with regard to concurrent adsorption processes.

The fact that on the one hand FR studies of mesoporous materials are rare, and on the other hand sulfated zirconium dioxides represent a relevant class of acidic heterogeneous catalysts with mesopores, represents the initial point of this study.

When checking the suitability of a homemade instrument for investigating certain phenomena, preliminary tests are necessary. Therefore, the first question to be answered was whether mesoporous materials are accessible using the existing frequency response apparatus. The FR results were then evaluated using various models in order to draw conclusions about the mass transfer processes taking place within the pore system of sulfated zirconium dioxide.

In order to know the conditions prevailing in the solid/gas system and to be able to interpret a FR spectrum, it is essential to characterize the porous material and to investigate adsorption using further methods. For this purpose, common techniques (adsorption isotherms, BET, and BJH analysis) and DRIFT spectroscopy were used in this study to accompany FR results.

DRIFT (diffuse reflectance infrared Fourier transform) spectroscopy is a powerful method with major benefits investigating the adsorption of gases on catalysts. In contrast to transmission FTIR spectroscopy, this method is non-invasive and can be used to follow the adsorption processes between the surface of the powdered catalyst and the adsorptive *in situ* under reaction conditions similar to the catalytic bed architecture.[17] To date, there are only a few DRIFTS studies that deal with the adsorption of light alkanes on SZ[18] – with the exception of *n*-butane, which has been extensively studied using both DRIFTS and other methods.[19–21] In the present work, the adsorption and diffusion behavior of short-chain alkanes (ethane, propane, iso-butane, *n*-butane, and neopentane) on SZ was investigated with a view to targeted catalyst development in the field of hydrogenation reactions and a deeper understanding of the interactions between these alkanes and the SZ surface. Building on this work, various mesoporous materials are planned to be examined and compared with each other.

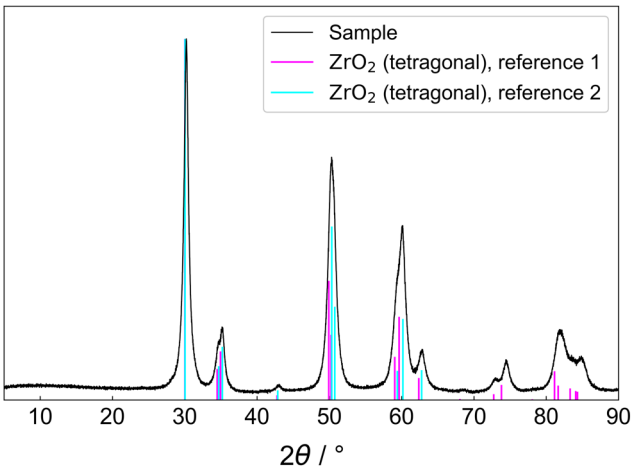

Fig. 1 Powder X-ray diffractogram of sulfated zirconia with XRD pattern of two references for tetragonal zircona.[22,23]

Results and discussion

Powder X-ray diffraction (XRD)

Powder XRD measurements were performed to investigate the crystal structure of the synthesized SZ sample used for FR. The recorded diffractogram as well as the reflexes characteristic of tetragonal zirconium(IV) oxide are shown in Fig. 1.

Based on the matching XRD patterns of the sample and the references, the tetragonal structure of the SZ sample is confirmed. From this it can be concluded that calcination at 600 °C stabilizes the catalytically active tetragonal crystal modification of SZ at room temperature.

Nitrogen adsorption isotherm for pore analysis

The nitrogen adsorption isotherm of the SZ sample at a temperature of −196 °C, displayed in Fig. 2, results in a type IV isotherm with hysteresis loop of type H2(b) according to IUPAC.[24]

The shape of the nitrogen isotherm and the results of the physisorption analysis, summarized in Table 1, confirm the mesoporous character of the SZ sample. The mesopores, which

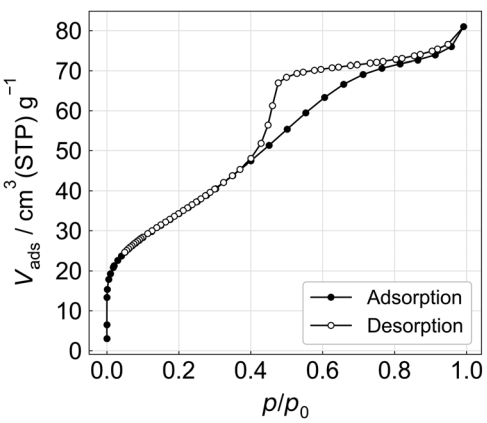

Fig. 2 Adsorption and desorption isotherm of nitrogen for SZ at −196 °C.

Table 1 Results of nitrogen physisorption analysis of the SZ sample

Analysis	Details	Results
Multi point BET	A_{spez}/m^2 g^{-1}	130
	C	62
Gurvich rule	V_{por}/cm^3 g^{-1}	0.12
	p/p_0	0.95
BJH (desorption, Harkins–Jura)	Median d_{por}/nm	3.30
	V_{por}/cm^3 g^{-1}	0.13

have a median diameter of 3.30 nm, dominate the pore system of the material.

Taking into account the molecular diameters of the adsorptives and the measurement conditions during the FR analysis (pressure and temperature), this pore size of SZ leads to Knudsen numbers between approx. 270 and 630, hence clearly in the Knudsen regime.

Densities and particle size distribution

Table 2 lists the specific densities of SZ and Fig. 3 shows the actual particle size distribution, both exemplified by the grain size fraction 150–250 µm.

Alkane adsorption isotherms

Fig. 4 illustrates the adsorption isotherms of ethane, propane, iso-butane, and *n*-butane with SZ at a temperature of 35 °C. The variable adsorption ability of the gases are evident: The adsorption capacity of SZ increases with increasing chain length of the alkane.

The pressure range relevant for the FR investigation is approx. 2.5 kPa. This is a compromise between the technical resolution of the equipment and the steepest possible (and ideally linear) range of the isotherms. Comparing the initial slopes of the isotherms, it is noticeable that the adsorption isotherms of the C_4 alkanes are quite similar to each other, even though they differ in terms of their loading as they progress.

Table 2 Densities of a SZ sample

Details	Results
Bulk density/g cm^{-3}	1.05
Particle density/g cm^{-3}	2.70
Skeletal density/g cm^{-3}	4.33

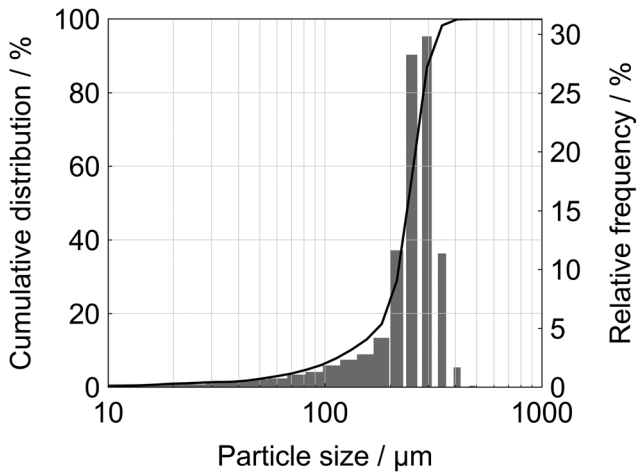

Fig. 3 Cumulative distribution curve (left axis of ordinate) and histogram (right axis of ordinate) of particle diameters of a SZ sample.

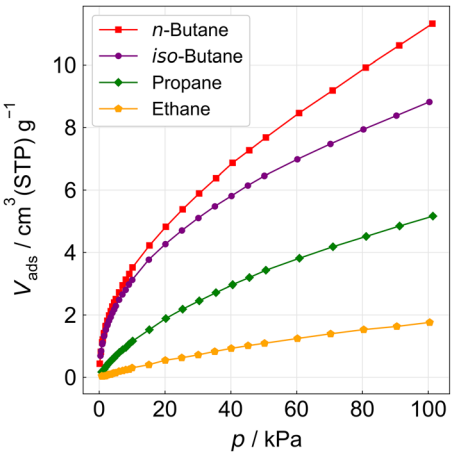

Fig. 4 Adsorption isotherms of C_2–C_4 alkanes with SZ at 35 °C.

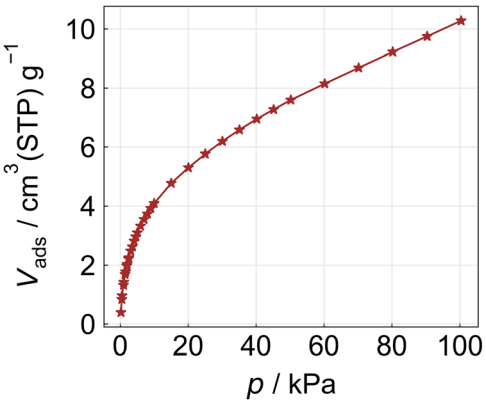

Fig. 5 Adsorption isotherm of neopentane with SZ at 35 °C.

The adsorption isotherm of neopentane with SZ of a second grain fraction is shown in Fig. 5. With regard to the final loading of more than 10 cm^3 (STP) g^{-1} at a pressure of 100 kPa, this adsorptive ranks in the order of magnitude of *n*-butane. The shape of the isotherm curve (and thus also the gradient in the very low pressure range) is also similar to that of the C_4 alkanes.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

Adsorption and desorption behavior of the alkanes ethane, propane, iso-butane, *n*-butane, and neopentane on SZ was investigated using DRIFT spectroscopy. As an example, Fig. 6 shows the spectra before adsorption, after adsorption, after purging with nitrogen and after desorption of propane on SZ in the wavenumber range from 4000 to 500 cm^{-1}. All alkanes show similar qualitative adsorption behavior and therefore, the

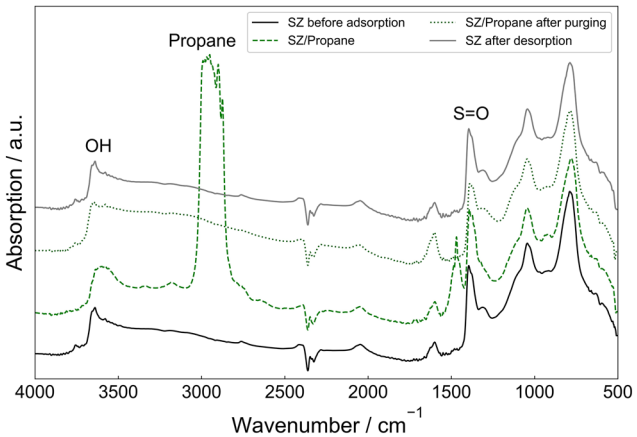

Fig. 6 DRIFT spectra of SZ before adsorption, with adsorbed propane, with adsorbed propane after purging and after desorption at 35 °C.

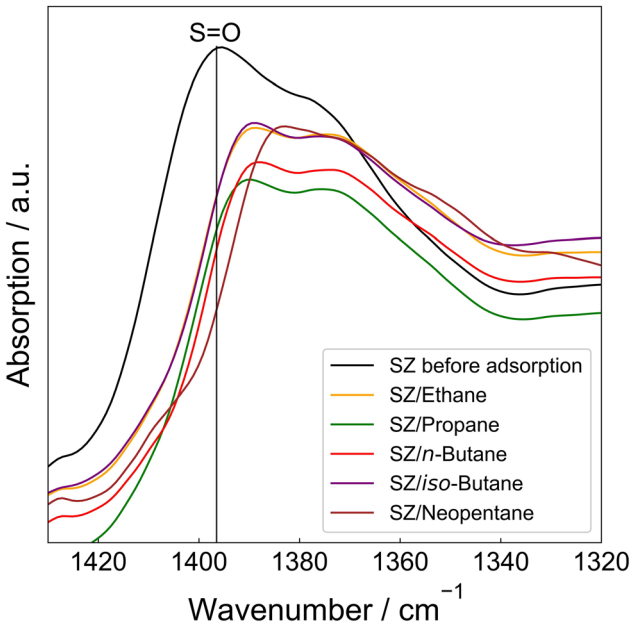

Fig. 7 DRIFT spectra of sulfate band region at around 1400 cm^{-1} of pure SZ before adsorption and SZ with adsorbed ethane, propane, *n*-butane, iso-butane, and neopentane.

spectra differ only slightly. Thus, the spectra of propane, which are not yet found in the literature in this form, are shown here as a representative of the test series. The DRIFT spectra of SZ with ethane, iso-butane, *n*-butane, and neopentane can be found in the Supplementary Information.

The spectra in Fig. 6 clearly show the changes during adsorption in several wavelength ranges: On the one hand, the hydroxyl region at higher wavenumbers between 3800 and 3400 cm^{-1}, which can be assigned to the terminal OH groups of the sulfated tetragonal ZrO_2 surface, is red shifted and the band shape changes to a broader band without a clear maximum. In addition, the disulfate band at approx. 1400 cm^{-1} is shifted to lower wavenumbers and clearly indicates the adsorption of propane on the SZ surface. After purging with nitrogen, this band is still shifted, indicating chemisorption. The spectrum after desorption by heating up to 400 °C corresponds again to the initial spectrum; propane was completely desorbed.

Fig. 7 illustrates in more detail the active band in isomerization catalysis, *e.g.*, the disulfate band at 1400 cm^{-1}, before and after adsorption for all alkanes.[19] This band, which is recognized by its characteristic double band structure, is related to the vibration of the S=O stretching mode and plays a central role in the adsorption process of *n*-butane.[25] Moreover, depending on the mechanisms, other alkanes may also adsorb here. During adsorption, the band shifts to lower wavenumbers (red shift) and its intensity decreases. Even after saturation of the surface and removal of physically adsorbed alkanes, this change remains, which clearly indicates chemisorption of the alkanes to this structural group.

All alkanes show a red shift of the disulfate band, however with slight differences. While ethane, propane, and iso-butane show a slight shift in the sulfate band, *n*-butane and neopentane exhibit a greater red shift. Nevertheless, it can be concluded that all alkanes possess a quite similar adsorption behavior. It can be assumed that adsorption is stronger with increasing chain length.[18,26] This correlation is currently being investigated and verified with theoretical calculations and will be further discussed in a subsequent paper.

Frequency response

Preliminary investigations. Argon was used as non-adsorbing tracer prior to the measurements with alkanes on SZ. In addition, comparative measurements with various adsorptives (including nitrogen and methane) were carried out for another mesoporous material (ordered silica MCM-41, A_{spez} = 540 m^2 g^{-1} (BET), V_{por} = 0.38 cm^3 g^{-1} (Gurvich), Median d_{por} = 2.47 nm (BJH)).[27] It was found that combinations with gases with only weak adsorption characteristics (SZ/argon, MCM-41/nitrogen, and MCM-41/methane) result in invalid FR spectra (poor signal to noise ratio). Unlike Reyes' method,[11] a certain extent of adsorption ability is therefore a condition for the selection of adsorptives for an adequate frequency response usage.

The sample configuration used was a packed bed of coarser grains of SZ interwoven with stainless steel wool. The FR transparency of this wool was confirmed by an FR measurement with *n*-butane in advance.

In order to identify bed effects, the SZ sample was compressed into tablets and analyzed under the same conditions as the bed configuration. Analog pressure responses were obtained in comparison to the tests with grain size fractions, which led to the conclusion that bed effects are not to be expected with the present method.

The FR spectra of SZ/argon, MCM-41/nitrogen, MCM-41/methane, and stainless steel wool/*n*-butane are compiled in the Supplementary Information. Furthermore, a replicate run of SZ/propane can be found there, which proves the qualitative repeatability of the FR measurements.

Theoretical background. The frequency response measurements of SZ with alkanes were evaluated according to the methodology already described.[9] The FR results described in

the following are presented as the so-called characteristic FR functions: A plot of two coupled functions (''in-phase'' and ''out-of-phase'', left part of eqn (1) and (2), respectively), in which the amplitude ratio of an FR measurement without and with adsorbent (p_B/p_Z) and the phase shift between measurement and blank measurement (ϕ_{Z-B}) are included, over the frequency of the volume modulation.

The FR measurements of sulfated zirconia resulted in monomodal curves of the characteristic functions (see Fig. 8): only a single resonance peak occurs in the form of an inflection point of the in-phase function and a maximum of the out-of-phase function. In terms of the ''detection window'' which the present method spans with its individual frequency range, one can interpret this as follows: (i) a single mass transfer process is resonating or (ii) multiple independent processes are resonating, but their time constants (reciprocal of the resonance frequency) are sufficiently similar resulting in a joint FR peak. Reyes *et al.* extended these scenarios by a third option:[11] in the case of a mesoporous material, a monomodal shape of the FR curves can also result from coupled diffusion and adsorption phenomena. To this end, they developed a theoretical model based on a transfer function that considers the following limiting cases:

- Diffusion rate » adsorption rate: decoupling of diffusion and adsorption leads to two separate FR peaks (resonance of diffusion at high frequencies, resonance of adsorption at low frequencies)
- Diffusion rate « adsorption rate: resonance peaks overlap so that FR spectrum resembles a pure diffusion spectrum (leading to a diffusion-like spectrum), ''apparent'' diffusion coefficient is obtained.

A pure diffusion spectrum is typically characterized by the in-phase and out-of-phase curves approaching each other asymptotically in the high frequency range.[16] In a characteristic adsorption FR spectrum, the curves ideally intersect at the maximum of the out-of-phase curve.[4] An intermediate scenario

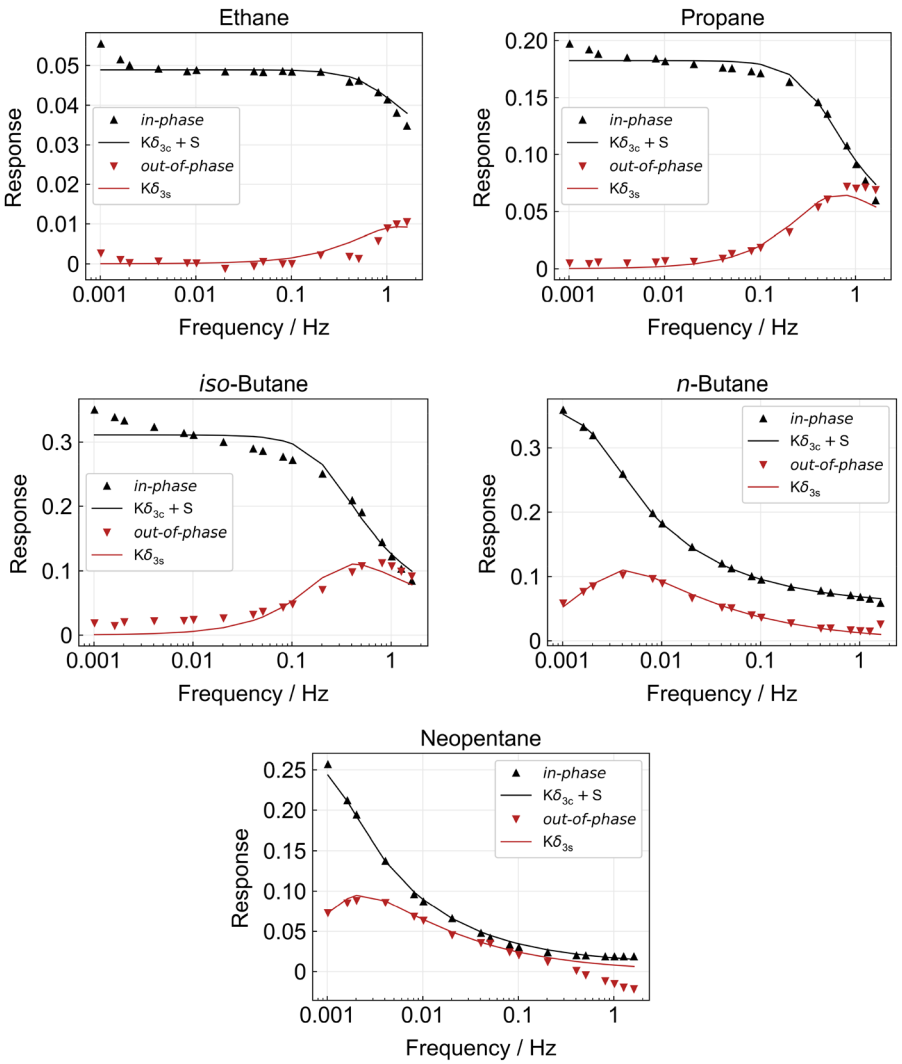

Fig. 8 FR spectra of SZ/ethane (θ = 35 °C, p = 2,4 kPa, m = 1891 mg), SZ/propane (θ = 35 °C, p = 2,3 kPa, m = 1891 mg), SZ/iso-butane (θ = 35 °C, p = 2,6 kPa, m = 1891 mg), SZ/n-butane (θ = 35 °C, p = 2,5 kPa, m = 1891 mg), and SZ/neopentane (θ = 35 °C, p = 2,5 kPa, m = 1249 mg) with experimental values (symbols) and model fits (Yasuda's diffusion model, lines).

between the two limiting cases of the coupled model is characterized by comparable diffusion and adsorption rates, both contributing considerably to the frequency response of the system. Reyes' model follows the principle whereby in materials with mesopores and a high specific surface area, a distinction can be made between the intracrystalline gas phase and the adsorbed phase – in contrast to microporous systems. The adsorption process is considered to follow Langmuir's kinetic.

Analysis of sulfated zirconia with alkanes. Since most of the obtained FR results are typical diffusion FR spectra, Yasuda's diffusion model was firstly applied.[16] The occurrence of only one FR peak is attributed to intraparticle diffusion. The theoretical model allows a diffusion coefficient to be extracted assuming isothermal diffusion of a species into an isotropic sphere following Fick's second law. The in-phase and out-of-phase curves are fitted by the model equations in the right part of eqn (1) and (2):

$$\frac{p_B}{p_Z}\cos\phi_{Z-B} - 1 = K\delta_{3c} + S \quad (1)$$

$$\frac{p_B}{p_Z}\sin\phi_{Z-B} = K\delta_{3s} \quad (2)$$

For the model equations – as for the rest of the study – the primary references should be sought. The diffusion time constant $\tau = R^2/D$ (with characteristic radius R of the spherical particle and effective diffusion coefficient D_{eff} in this case), the capacity value K and S as an additional constant of the in-phase component are obtained as fit parameters. S can be interpreted as adsorption/desorption process occurring fast and simultaneously to diffusion[28,29] or it is considered as an additional intercrystalline diffusion process.[16,30]

Fig. 8 summarizes the FR spectra of SZ in interaction with ethane, propane, iso-butane, *n*-butane, and neopentane along with the fits of Yasuda's diffusion model. The resulting parameters can be found in Table 3.

The intensity of the FR signal (indicated by the value of the in-phase function, idealized at a frequency of 0 Hz) corresponds in this case to the sum of K and S. K is proportional to the slope of the isotherms in the relevant pressure range of the FR measurement.[10,16] This value represents the storage capacity of the adsorbent for the respective type of adsorptive. In order to check the applied model for plausibility, the coefficient K can be compared with the corresponding value K_{iso} determined from the gradient of the isotherms at the respective point of the measurement pressure (see Table 3). Except for SZ/propane, these values coincide in good approximation, which allows the conclusion that the diffusion model according to Yasuda captures the mass transfer processes taking place in the grains of sulfated zirconium dioxide to a high degree – on the basis of an effective intraparticle diffusion coefficient D_{eff}. This diffusion coefficient was calculated by using the actual median particle size, since nearly spherical grains of sulfated zirconia are used (median circularity 0.87) and the condition of an idealized spherical geometry of the adsorbent is thus considered to be fulfilled. Since the theoretical Knudsen diffusion coefficients lie within 3.3–5.1 $\times$ 10^{-7} m^2 s^{-1} under the prevailing conditions, it is striking that the diffusivities obtained lie outside the Knudsen regime. This may be plausible in so far as intraparticle diffusion processes in mesopores are formally expected in the Knudsen regime, but with Yasuda's model, effective diffusivities are obtained. DRIFTS proved chemisorption phenomena in the investigated solid/gas systems, as a ''regeneration'' of the relevant IR bands of SZ by desorption was only possible at high temperatures. Such strong adsorption effects may inhibit intraparticle mass transfer or result in significantly lower diffusion coefficients if an integral analysis of the FR response is performed. Another key factor here is the tortuosity of the SZ sample. The actual pore size distribution and pore network effects affect the diffusion within the pore network. However, this aspect should only be determined on the basis of extensive tests, since tortuosity values and correction factors are subjects of scientific discourse.[31–33]

The factor S from Yasuda's model is extremely low for the systems SZ/propane and SZ/iso-butane. These combinations also result in characteristic FR functions that deviate from the typical shape of a pure diffusion spectrum, and they show a noticeable deviation of the theoretical model from the data points in the area of the resonance peak. A potential intersection of the curves cannot, by nature, be depicted by Yasuda's diffusion model, but could be taken as an indication for the influence of adsorption. For this reason, the coupled adsorption and diffusion FR model according to Reyes[11] was applied as a second option to all spectra: A transfer function ($H(i\omega)$ with the angular modulation frequency ω), which takes into account adsorption and diffusion as a dynamic and a capacity parameter each, was curve-fitted to the in-phase and out-of-phase functions according to eqn (3) and (4) as real part (RRF, real response function) and imaginary part (IRF, imaginary response functions) respectively:

$$RRF = Re\left(\frac{1}{H(i\omega)} - 1\right) \quad (3)$$

Table 3 Dynamic and capacity parameters of sulfated zirconia with light alkanes

	Yasuda's diffusion model				From isotherms	Reyes' model: diffusion and adsorption coupled			
Samples	τ/s	K/—	S/—	D_{eff}/m^2 s^{-1}	K_{iso}/—	D/m^2 s^{-1}	K_g/—	k_r/s^{-1}	K_S/—
SZ/ethane	1.34	0.03	2.3×10^{-2}	1.3×10^{-8}	0.03				
SZ/propane	2.69	0.18	2.5×10^{-12}	6.4×10^{-9}	0.12	6.4×10^{-7}	1.0×10^{-3}	20	0.16
SZ/iso-butane	4.32	0.31	6.9×10^{-22}	4.0×10^{-9}	0.29	4.8×10^{-7}	1.2×10^{-3}	36	0.29
SZ/*n*-butane	428	0.31	5.6×10^{-2}	4.0×10^{-11}	0.32				
SZ/neopentane	785	0.27	8.8×10^{-3}	4.2×10^{-11}	0.28				

$$\mathrm{IRF} = -\mathrm{Im}\left(\frac{1}{H(\mathrm{i}\omega)} - 1\right) \quad (4)$$

The fit parameters obtained here are D (intraparticle diffusion coefficient), K_g (capacity of the intraparticle gas phase following ideal gas law), K_S (adsorption capacity) and k_r (adsorption relaxation frequency), see Table 3. For SZ/ethane, SZ/*n*-butane, and SZ/neopentane, the application of the "diffusion-like" limiting case of the model is appropriate, which results in nearly identical values as from Yasuda's model, as long as an additive constant is also introduced here. Consequently, the diffusive character predominates in these measurements. For SZ/propane and SZ/iso-butane, the coupled model captures the intersection of the in-phase and out-of-phase functions (Fig. 9), thus providing a better representation of the qualitative curve shape of the characteristic functions. In contrast, the modeling of the response in the low frequency range is poorer. It should be noted that Reyes *et al.* only investigated a frequency range starting from 0.1 Hz. The lower frequency range of mesoporous materials has not yet been explored using VSFR and requires more in-depth investigations. Low-frequency thermal or instrumental drifts are not assumed to bias the fits; on the one hand, because corresponding blank measurements are included in the evaluation (and thus, effects such as compression heat of the sample gas are eliminated), and on the other hand, because only the frequency of the volume modulation is included in the calculation of the characteristic FR functions, so that disturbances with a frequency other than the primary frequency are not taken into account for the evaluation.

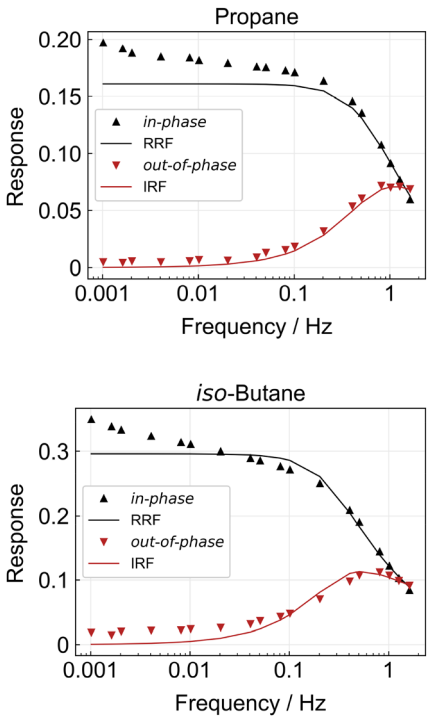

Fig. 9 FR spectra of SZ/propane (θ = 35 °C, p = 2,3 kPa, m = 1891 mg) and SZ/iso-butane (θ = 35 °C, p = 2,6 kPa, m = 1891 mg) with experimental values (symbols) and model fits (Reyes' coupled model, lines).

The separation of diffusion and adsorption for SZ/propane and SZ/iso-butane leads to diffusion coefficients D in the Knudsen regime (theoretical values: SZ/propane 4.2×10^{-7} m^2 s^{-1}, SZ/iso-butane 3.7×10^{-7} m^2 s^{-1}), but also to adsorption capacities K_S, which in turn correspond well with the K_{iso} values from the isotherms.

The reasons why the adsorption character is more pronounced for SZ/propane and SZ/iso-butane than for the other systems investigated, when chemisorption was found to occur for all combinations, could not be clarified within this study. The aim was firstly to determine whether mesoporous materials are accessible with the existing apparatus and whether available models are able to provide reasonable conclusions about interparticle mass transfer processes. Both discussed models provide values whose feasibility was confirmed by the capacity values. While effective diffusion coefficients are obtained with Yasuda's diffusion model, Reyes' model allows the separate detection of adsorption and diffusion in the intraparticle gas phase, which leads to diffusion coefficients in the Knudsen regime.

Experimental

Sample material

The synthesis of sulfated zirconia (SZ) was described in detail in former papers.[34,35] Zirconium dioxide synthesized from zirconyl nitrate *via* precipitation and drying was mixed with an appropriate amount of dissolved ammonium sulfate and finally also dried. In order to stabilize the tetragonal modification of zirconia and to anchor the sulfate groups on the surface, the sample was subsequently calcined at 600 °C for 3 h under synthetic air flow (0.2 l min^{-1}). The nominal sulfate content of the SZ sample was 6 wt%. Elemental analysis was used to determine a mean sulfate content of 3.9 wt%.

In order to carry out the frequency response measurement, it was necessary to compact the sample material into coarse grains and sieve it to a specific grain fraction. Sieves of 150 and 250 µm or 250 and 300 µm were used for this purpose. The actual particle size diameter (median) and particle shape parameters of a grain fraction were determined by light scattering in combination with dynamic image analysis in water (Bettersizer S3 Plus) by 3P Instruments GmbH, Germany.

The particle density was determined *via* mercury porosimetry (Poremaster 60-GT, Quantachrome, USA) by 3P Instruments GmbH, Germany, and the skeletal density *via* helium pycnometry (AccuPyc II 1345, Micromeritics GmbH, Germany).

Gases of purity 2.0 (neopentane, Linde GmbH, Germany), 2.5 (iso-butane and *n*-butane, both Linde GmbH, Germany), 3.5 (ethane and propane, both Messer Industriegase GmbH, Germany), 4.5 (methane, Messer Industriegase GmbH, Germany), and 5.0 (argon, Messer Industriegase GmbH, Germany, helium and nitrogen, both Nippon Gases Deutschland GmbH, Germany) were used for the measurements.

Characterization

Powder X-ray diffraction (XRD). The powder XRD pattern of calcined sulfated zirconia was collected in Bragg–Brentano

geometry using an X'Pert Pro diffractometer (PANalytical GmbH, Germany) with a curved Ge-(111) monochromator and a PIXcel 1D detector (active length 3.3482°) using CuKα1 radiation (λ = 1.54059 Å) at ambient temperature between 5 and 90° 2theta.

Adsorption isotherms. The adsorption isotherms of nitrogen at a temperature of −196 °C for pore characterization and of alkanes at a temperature of 35 °C were recorded with a volumetric sorption analyzer (BELSORP Mini X, Microtrac Retsch GmbH, Germany). A pressure variation of ±1% (nitrogen) or ±0.5% (alkanes) for a duration of 180 s was selected as equilibrium condition. The samples were pretreated *in situ* at 300 °C for 5 h with a ramp of 1 K min^{-1}. Helium was used to calibrate the volume of the sample cells.

The Brunauer, Emmett, and Teller (BET) model was applied to the adsorption isotherm of nitrogen at −196 °C to obtain the specific surface area of the SZ sample.[36] In order to determine the pore volume, the relationship known as the Gurvich rule was used.[37] For the mesopore analysis, the method according to Barrett, Joyner, and Halenda (BJH) was applied.[38]

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

DRIFTS measurements were carried out using a Bruker Vertex 80 v FTIR spectrometer (Bruker Optik GmbH, Germany) with Praying Mantis Accessory (Harrick Scientific Products, USA) and a high temperature reaction chamber (Harrick Scientific Products, USA). As background for the experimental measurements, spectra of ground KBr were used. The SZ samples (200 mg, not diluted with KBr) were ground and then activated in the reaction chamber at a temperature of 400 °C for 1 h with 0.1 l min^{-1} nitrogen purging. The adsorption of ethane, propane, iso-butane, *n*-butane, and neopentane was carried out separately at a temperature of 35 °C for 5 min with a gas flow of 0.1 l min^{-1}. After the adsorption step, the sample was purged with nitrogen (30 min, 0.1 l min^{-1}) to remove physisorbed and non-adsorbed gas molecules. The desorption step involved heating the sample up to 400 °C with a heating rate of 10 K min^{-1} while purging with nitrogen. Spectra were recorded with a spectral resolution of 2 cm^{-1} and 32 averaged scans. The wavenumber range was 8000 to 500 cm^{-1}. The analysis of the spectra was done with OPUS software version 8.1 (Bruker Optik GmbH, Germany).

Frequency response

The FR setup has already been described in detail in previous studies.[8,9,39] The solid/gas system is exposed to a periodic volume variation of approx. ±1% at different frequencies (0.001–1.6 Hz). The resulting pressure change in the gas phase is detected over time. Since the present FR method applies a rectangular perturbation function, the pressure response is subjected to a Fourier transformation.

Each FR measurement requires a corresponding blank measurement in which no adsorbent is used, in order to exclude effects of device-specific artifacts and instrumental delays on the measurement result.

As sample configuration, the grains of SZ were used as a bed, which was interspersed with stainless steel wool (Rakso, stainless steel wool fine, Oscar Weil GmbH, Germany). The benefit of using stainless steel wool comes from affecting the porosity of the bed in a negligible way, but favoring the transport of potentially emerging adsorption heat, allowing isothermal conditions to be assumed. The FR tests were carried out at a pressure of approx. 2.5 kPa at a temperature of 35 °C.

A Python script based on NumPy was used to obtain the characteristic FR functions from the measured pressure response by means of Fourier transform.[40] For the curve fitting using the non-linear least squares curve fitting method, a Python script based on SciPy was programmed.[41]

Conclusions

To the best of our knowledge, this study is the first applying Reyes' frequency response model for coupled adsorption and diffusion in mesopores to an own VSFR method.[11] Thereby, the systematic exploration of the class of mesoporous materials by FR shall be enhanced. The methodical coupling of FR with DRIFTS is intended to demonstrate how broadly adsorption and diffusion can be investigated.

For this purpose, sulfated zirconia (SZ) was selected as a demanding heterogeneous catalyst and short-chain alkanes (ethane, propane, iso-butane, *n*-butane, and neopentane) were chosen as adsorptives. Sulfated zirconium dioxide was synthesized and thoroughly characterized. DRIFTS measurements, in which the alkanes were individually adsorbed *in situ* and then desorbed by purging and heating, indicated chemisorption effects.

In addition, FR tests were carried out with SZ and the alkanes. A fixed bed of coarse grains of SZ interspersed with stainless steel wool was used as sample configuration. All frequency response tests resulted in monomodal characteristics FR curves. The FR spectra were examined in more detail using two models. It was found that a basic diffusion model describes the occurring mass transfer processes to a high degree by means of an effective intraparticle diffusion coefficient. For the cases SZ/ethane, SZ/*n*-butane, and SZ/neopentane, the diffusion character was prevalent, but for SZ/propane and SZ/iso-butane the FR spectra showed features typical for adsorption, whereupon the model according to Reyes *et al.* was applied. By separately considering the intraparticle gas phase in the mesopores and the adsorbed phase with their own capacity and dynamic terms each, it was possible to distinguish between adsorption and diffusion in these systems. Modeling the relevant resonance peaks was qualitatively improved by this model in comparison to the simplified diffusion model, and diffusivities in the Knudsen regime were obtained. The comparison with the capacity value derived from the adsorption isotherms confirmed the plausibility of all modeling cases.

The presented approach offers a promising entry in the field of studying diffusion and adsorption processes in mesoporous catalysts such as sulfated zirconia by FR and DRIFTS.

Systematic test series for a more detailed characterization of the mass transfer processes of gases taking place in SZ and other mesoporous solids are to be carried out in the future using the methodology presented.

Author contributions

Conceptualization, R. G., M. G. and C. B.; methodology, R. G., M.G. and C. B.; software, R. G. and M. G.; validation, R. G. and M. G.; formal analysis, R. G. and M. G.; investigation, R. G. and M. G; resources R. G. and M. G; data curation, R. G., M. G. and C. B.; writing – original draft preparation, R. G. and M. G.; writing – review and editing, R. G., M. G. and C. B.; visualization, R. G. and M. G.; supervision, C. B.; project administration, C. B. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: additional FR spectra and DRIFT spectra. See DOI: https://doi.org/10.1039/d5cp02927a.

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