

A transient TAP study of the adsorption of C₄-hydrocarbons on sulfated zirconias

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Abstract

The interaction of C₄-hydrocarbons with the surface of two sulfated zirconias of considerable different catalytic activity has been investigated by using the temporal analysis of products (TAP) reactor. *n*-Butane and *iso*-butane as reactant and product molecules for the isomerization showed differences in their interaction with the surface of sulfated zirconia thus indicating slightly variable sorption features for both molecules. 1-Butene, as representative for a possible reaction intermediate or side product, had compared to the saturated C₄-molecules stronger adsorption abilities and desorbed slower from the surface of sulfated zirconia, which may also influence the sorption properties of *n*-butane and *iso*-butane during the catalytic cycle. Heats of adsorption from van't Hoff plots were modelled for *n*-butane and *iso*-butane and are comparable to calorimetry data for this system thus giving the opportunity to model the first step in a microkinetic model appropriately.

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1. Introduction

Transient measurements in a temporal analysis of products (TAP) reactor are a very fast and convenient way to determine the adsorption and desorption properties of gaseous probe molecules on catalytic active surfaces [1]. Sorption experiments are used to determine diffusion constants, adsorption and desorption constants as well as activation energies [2,3]. Moreover, transient studies allow a detailed view to microkinetics as they are able to focus on the investigation of single reaction steps. Only a limited number of transient studies exist which focus on the adsorption of alkanes on solid surfaces [4,5]. So far no TAP study is known regarding the alkane interaction with sulfated zirconias and the modelling of their adsorption.

This paper deals with the description of the adsorption and desorption properties of the main reactant and product molecules of the *n*-butane isomerization reaction. Isomerization is studied over the surface of sulfated zirconia, which is known to catalyze the isomerization at low temperatures [6]. Moreover, two samples of considerable different activity towards *iso*-butane formation were chosen to compare the adsorptive interaction of C₄-hydrocarbons on them.

The activation of alkanes on the surface of sulfated zirconias is still under discussion [7]. Adsorption is the first and main important step in the microkinetics of this process. Therefore, a detailed investigation of this activation step should give more insights regarding the general mechanism of alkane activation on sulfated zirconias and an adequate description of the adsorption step will be the starting point for an appropriate kinetic model to come. Heats of adsorption resulting from van't Hoff plots will be compared for the probe molecules *n*-butane and *iso*-butane on the surface of sulfated zirconia with variable activities.

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2. Experimental

2.1. Preparation of sulfated zirconia

The sulfated zirconias were prepared through precipitation from zirconyl nitrate solution with ammonia to a final pH of 8.4. The zirconias were aged either for 1 h at room temperature (series 1) or for 24 h at 373 K (series 2). The precipitates were washed and dried (24 h at 393 K) resulting in two precursors referred to as P1 and P2. Both precursor materials were sulfated by suspending them in a solution of ammonium sulfate (theoretical Zr:S ratio of 1:5). The sulfated materials were dried 24 h at 373 K. Calcination of the material (2 g) was done in a vertical reactor with a constant flow of air (30 ml min⁻¹) for 3 h at 873 K giving the catalyst materials C1 and C2, respectively. For comparison an industrial reference material from MEL Chemicals (XZO-620) was used and is referred here as C3. The unsulfated precursors were also calcined under the same conditions and are named P1 and P2, respectively.

2.2. TAP experiments

Temporal analysis of products (TAP) was conducted in a TAP-2 system [8] in the temperature range 323–523 K. Samples were activated before use in TAP at 573 K for 2 h in vacuum in the microreactor. Fresh samples (100 mg) were exposed to single pulses of *n*-butane, *iso*-butane and 1-butene. The gases employed were *n*-butane (99.5 vol.%, Messer), *iso*-butane (99.95 vol.%, Fluka), 1-butene (99.0 vol.%, Messer). Different inert reference gases were used (He, Ar) for comparison. In first measurements helium was used (323–523 K for the precursors and catalysts). Also measurements with argon (373–523 K for catalyst samples only) were performed to have a basis for a subsequent modelling procedure. It is reported that modelling Knudsen diffusion coefficients for helium is affected by its low molecular mass, which makes it unable as basis for the evaluation of adsorption and desorption constants [9]. Thus, all modelling procedures were done based on the argon measurements. It has to be noted that under the Knudsen diffusion regime the gases in a mixture do not interact thus the use of a special inert gas does not influence the measurement outcome at all. Pulses of a constant pulse width of 130 μ s were used and the reactant mixtures in the blending tank consisted of 50 mbar inert gas and 350 mbar reactant gas. An experiment consisted of several cycles of pulses with signal averaging (in general 10 pulses to improve the signal-to-noise ratio). The reactor bed was built up from inert material (corundum) of 400 mg, a catalyst section with 100 mg followed by inert material of 600 mg. The particle diameter for all materials was a sieve fraction of 0.1–0.315 mm as used in our catalysis experiments in the fixed bed reactor at atmospheric pressure. The temperature was controlled by a thermocouple positioned in the centre of the bed. The catalyst was heated to the measurement temperatures in vacuum at a rate of 10 K/min. The gas outlet from the reactor was detected by

a quadrupole mass spectrometer (QMS) from HIDEN, where single masses (m/e) of interest can be followed. All possible fragments for *n*-butane and *iso*-butane were monitored. Fragmentation patterns of the pure substances were recorded separately in a reactor filled with corundum ($d_p = 0.1$ – 0.3 mm). Only their main mass fragments $m/e = 27, 29, 41, 43, 58$ will be discussed in detail here. 1-Butene was mainly monitored at $m/e = 41, 56$.

Knudsen diffusion in the reactor during pulse experiments was ensured by controlling the pulse intensity of the responses. The shape of the response curves has to be independent from the pulse size. Pulse sizes were then kept constant.

Modelling was done by using the software by Schuurman [14], which gives estimates for adsorption and desorption rate constants. These values were used to calculate the equilibrium constant K . van't Hoff plots ($\ln K$ versus $1/T$) gave then estimates for heats of adsorption.

2.3. Characterization of the samples

Surface area measurements were performed with an ASAP-2000 (Micromeritics). For X-ray diffraction the powders were investigated with XRD-7-diffractometer (Seifert) using Cu K α radiation. The sulfur content was determined by elementary analysis [11]. For temperature-programmed desorption (TPD) of NH₃, the catalysts were exposed to NH₃ at 373 K with 300 μ l NH₃. Then the samples were heated at a rate of 10 K min⁻¹ and desorbing NH₃ was detected by MS ($m/e = 15$).

3. Results and discussion

3.1. Characterization

Table 1 summarizes the results from nitrogen sorption for the precursor and catalyst materials. The specific surface areas were calculated according the BET equation [16]. The pore size distributions were calculated by the Barrett–Joyner–Halenda (BJH) method [17]. The desorption branches were used for calculating the pore sizes. The unsulfated zirconias P1 and P2 exhibited only half of the surface areas of C1 and C2. It is well known that sulfation has a great influence on the formation of higher surface areas of zirconias [10]. Calcination of the sulfated samples resulted in a decrease in pore diameters and thus the surface areas were increased. C1 had a surface area of 103 m²/g, C2 one of 150 m²/g. The sulfate content for C1 was 9 wt.%, i.e. the number of sulfur atoms on the surface can be estimated to be

Table 1
Nitrogen sorption data for precursors P1, P2 and catalyst samples C1–C3

Sample	P1	C1	P2	C2	C3
BET (m ² /g)	48	103	86	150	122
Pore diameter (Å)	63	35	50	40	–

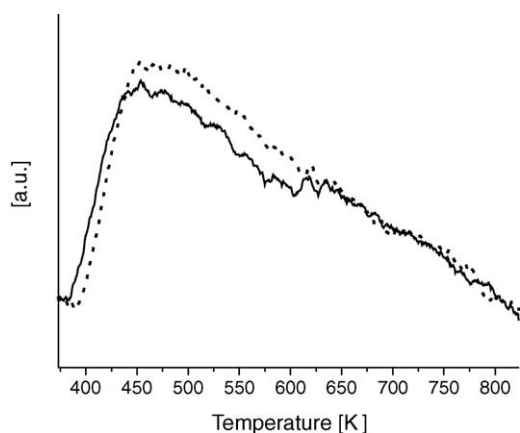


Fig. 1. Ammonia-TPD for catalyst materials C1 (—), C2 (···) (C1: $5.0 \times 10^{-3} \text{ mmol m}^{-2}$; C2: $3.2 \times 10^{-3} \text{ mmol m}^{-2}$).

$5.3 \times 10^{18} \text{ S-atoms/m}^2$. C2 had a comparable sulfate content of 8.9 wt.%, thus resulting in sulfur coverage of $3.7 \times 10^{18} \text{ S-atoms/m}^2$, which is therefore significantly smaller, compared to C1. The reference sample C3 had a sulfur content of 6.5 wt.% and the lowest sulfate coverage of $2.6 \times 10^{18} \text{ S-atoms/m}^2$.

The XRD data of C1–C3 (not presented here) showed typical diffraction peaks for the tetragonal phase of zirconia. They were mainly tetragonal with only a small monoclinic contribution [11].

The results from ammonia TPD are illustrated in Fig. 1. They do not show a significant difference for both samples. C1 and C2 exhibited the typical broad desorption profile for ammonia from sulfated zirconias. The concentration of acid sites can be estimated as 5.0×10^{-3} and $3.2 \times 10^{-3} \text{ mmol m}^{-2}$ for C1 and C2, respectively. As both samples had the same sulfur content this is a reasonable result.

The catalytic experiments are described in detail in a previous paper [11]. C1 had the highest activity towards *iso*-butane formation (conversion is 20% at 423 K) followed by rapid deactivation. C2 and C3 were not or less active and did not show long term stability. This significantly different catalytic behaviour of the samples C1 and C2 was quite interesting as they exhibited the same overall sulfur content, which should be related to the isomerization activity. But due to their different specific surface areas the sulfate group density seems to make the difference in the catalytic activity. The reason for this dependence is still not clear and under consideration [11]. These two samples were therefore an interesting starting point to investigate adsorption, desorption and reaction within a TAP experiment.

3.2. TAP—interaction with *n*-butane

TAP experiments were carried out for the first time to characterize the sorption abilities of sulfated zirconias while interacting with reactant and product molecules. Especially

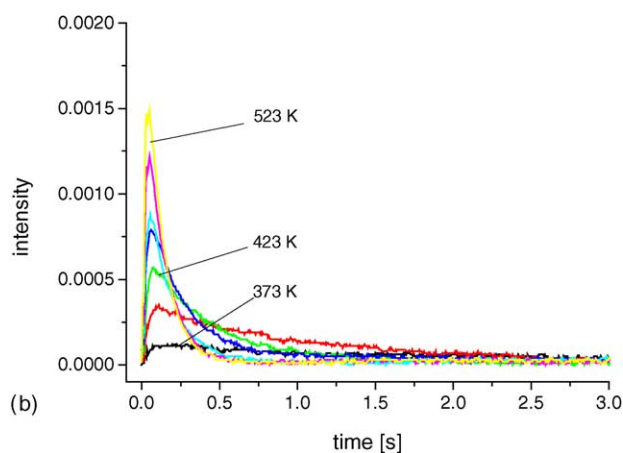
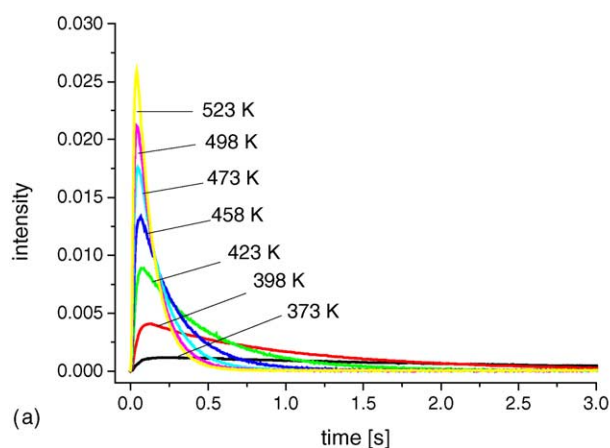


Fig. 2. Response curves for single pulses of *n*-butane over C1 for 373–523 K, inert reference argon: (a) $m/e = 43$; (b) $m/e = 58$.

of interest was the investigation and comparison of samples with differing porosity and catalytic activity.

The shapes of all curves indicated reversible adsorption behaviour of *n*-butane on the surface of sulfated zirconia, which is an important feature out of a TAP pulse experiment. Fig. 2 shows the response curves for pulsing *n*-butane over fresh C1. Argon was used as reference gas. From the response curves a strong adsorption of *n*-butane can be concluded. An extremely long desorption phase was observed for low temperatures. Measurements with Helium (not shown here, similar to the Argon outcomes) were first done also at 323 K. Here it could be observed a rather long desorption phase up to 30 s for the pulse response at 323 K. Therefore, a time interval for pulsing of up to 30 s was chosen to desorb the probe molecules totally.

Especially the relations between the observed intensities of $m/e = 58$ (parent peak) and $m/e = 43$ are shown in detail in Fig. 2. For both masses (43, 58) the same curve shapes were observed. The measured intensities of the response curves for $m/e = 43$ were much higher compared to those from $m/e = 58$, which corresponds to the intensity given by the general fragmentation pattern of C_4 -hydrocarbons in the MS which was observed over inert material, too.

In principle the trend of the response curves for the samples C2 and C3 with increasing temperature was similar (not shown here). C3 as reference catalyst was, however only investigated at 423 and 523 K. The absolute measured intensities for C2 and C3 varied compared to C1 indicating different surface interactions according to their catalytic activities.

It has to be noted that a TAP experiment is state defining, due to the very small number of molecules, which are pulsed during a cycle. Thus, the observed pulse responses for all samples correlate to a nearly unchanged catalyst surface. This would correspond to a time on stream in the very beginning of a catalysis experiment under atmospheric conditions.

Comparing all response curves in Fig. 2 it is obvious that the interaction of the probe gas changed with temperature. At low temperatures the adsorption of the probe molecule *n*-butane was rather strong. It took some seconds for the total desorption of the pulsed/converted molecules from the surface. Even at 423 K the adsorption was still strong. From 458 K up to 523 K the desorption time was shortened to less than 1 s and the process of diffusion governed the curve response shape. The curves tended to be narrower with increasing temperature.

A quantitative calculation of conversion of *n*-butane to *iso*-butane from TAP experiment is difficult because of the similar fragmentation pattern for *n*-butane and *iso*-butane in MS. It can be partly achieved by the comparison of fragment ratios instead of single fragment masses for different temperatures and samples. If the same processes, i.e. adsorption/reaction/desorption occur on the surface, similar fragmentation ratios should be observed. To calculate these fragmentation ratios the areas of the response curves were evaluated for each temperature and special response curve. It has to be noted that for masses with lower intensity the error in estimating these areas is higher through a lower signal-to-noise ratio.

For *iso*-butane especially $m/e = 43$ should be more pronounced through stabilization of this fragment. If we had a conversion of *n*-butane to *iso*-butane the general fragmentation ratio of $m/e = 43$ to 58 should be different in comparison to an inert standard. In Table 2 the observed fragmentation pattern for C1–C3 and those expected from pure *n*-butane and *iso*-butane over inert material are listed for comparison. Values for the range 373–423 K will be discussed in detail only.

C1 showed clearly a ratio above the average value of eight for pure *n*-butane measured with inert material. The values for C2 and C3 lay below the value of C1. As $m/e = 43$ should

Table 2

Comparison of fragmentation pattern $m/e = 43/m/e = 58$ for C1–C3 with inert reference argon with pure *n*-butane ($43/58 = 8$) and *iso*-butane ($43/58 = 25$) measured over inert material

Sample	373 K	398 K	423 K
C1	11.5	11.6	14.2
C2	6.6	8.3	7.5
C3	–	–	11.3

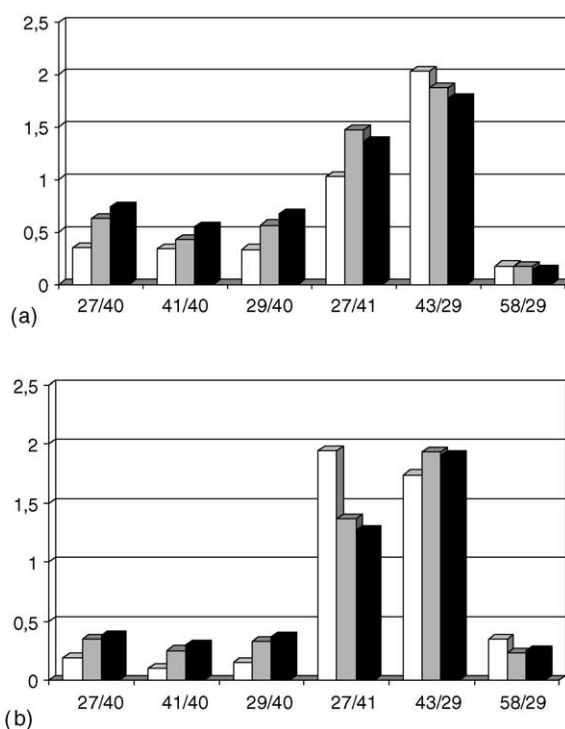


Fig. 3. Calculated fragmentation ratios: $m/e = 27/m/e = 40$; $m/e = 41/m/e = 40$; $m/e = 29/m/e = 40$; $m/e = 27/m/e = 41$; $m/e = 43/m/e = 29$; $m/e = 58/m/e = 29$.

be more pronounced for *iso*-butane this corresponds to the observed isomerization activity known from catalysis, i.e. C1 is active and C2 and C3 are not or less active and there was for the latter no change of the $m/e = 43$ to 58 ratios compared to the inert material. An increase in the fragmentation ratio with temperature, which would reflect a higher reaction rate according to a higher temperature, may not be so pronounced in the TAP response pulse as in a catalysis experiment because numerous simultaneous linked processes have to take into account. However, there was a small increase for C1 and C2 observable with temperature.

To confirm a different product formation or reactant adsorption/desorption on the surfaces of C1 and C2, additional fragmentation ratios are shown in Fig. 3. It is obvious that all fragment ratios of C1 and C2 varied in their absolute values and also in their order of appearance which supports different surface processes on C1 and C2 reflecting different activities of the catalysts as observed in the catalytic experiments. The fragments 27, 29 and 41 were chosen because they reflect those fragments, which exhibit the highest changes between *n*- and *iso*-butane when pulsed over inert reference material.

It is known that alkanes also adsorb on pure unsulfated zirconia surfaces [12]. Thus, to investigate the sorption behaviour of *n*-butane on the surface of the porous and inactive support material, P1 and P2 were investigated by pulsing reactant *n*-butane, too. As no conversion by pulsing *n*-butane over these precursors is expected, the interaction of the probe molecule should be only determined by the combined processes of adsorption, desorption and diffusion. Thus

Table 3
Residence times (s) for pulses of *n*-butane for P1 and P2, C1 and C2 calculated from the first moments of the response curves, inert reference gas used in brackets

Sample (K)	P1 (He)	P2 (He)	C1 (He)	C2 (He)	C1 (Ar)	C2 (Ar)
323	– ^a	9	18	13	–	–
348	2.7	4.9	8.5	8.9	–	–
373	1.8	1.5	5.5	2.7	–	–
398	0.83	0.78	1.54	0.88	1.05	1.08
423	0.40	0.39	0.53	0.40	0.50	0.45
448	0.23	0.27	0.28	0.24	0.28	0.26
473	0.19	0.19	0.17	0.16	0.19	0.17
498	0.18	0.15	0.14	0.14	0.15	–
523	0.17	0.13	0.12	0.12	0.13	0.12

^a Recording time was only 1 s, *n*-butane still desorbing, see Fig. 4.

all molecules in the response pulse can be attributed to *n*-butane. The duration of the *n*-butane interaction with the precursor surface can be estimated by the residence times. Residence times are available over momentum analysis of the response curves and are calculated as the first moments here [13]. For the experiments with the precursor materials Helium was used as reference gas, exceptionally. Also lower temperatures of 323 and 348 K were investigated in this case. Table 3 summarizes all residence times, calculated as first moments from the response curves [14]. To get a systematic overview the values calculated for C1 and C2 are listed, too. The range of the response curve, which was considered for the calculation (integration), varies depending on the desorption behaviour. This is especially important for the evaluation of the low temperature response curves because of the observed strong adsorption. The error made by an integration of curves with a low signal-to-noise ratio is around 5%. The principal trend was not affected at all. The slight differences between the C1 and C2 values for the Helium and Argon measurements lie within the error range and have no influence on the interpretation at all.

It can be seen that the residence times of *n*-butane on the catalysts changed dramatically with temperature. At low tem-

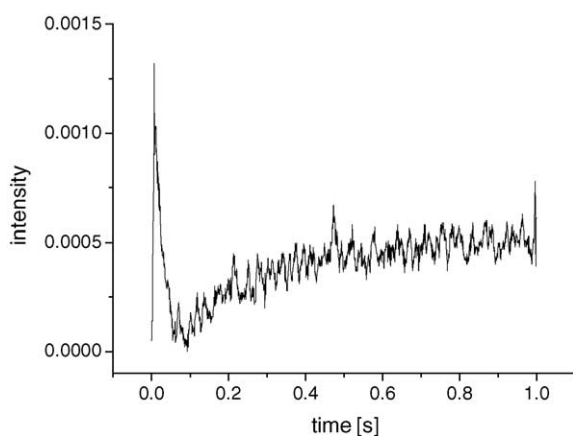


Fig. 4. Response curve for *n*-butane over P1 at 323 K.

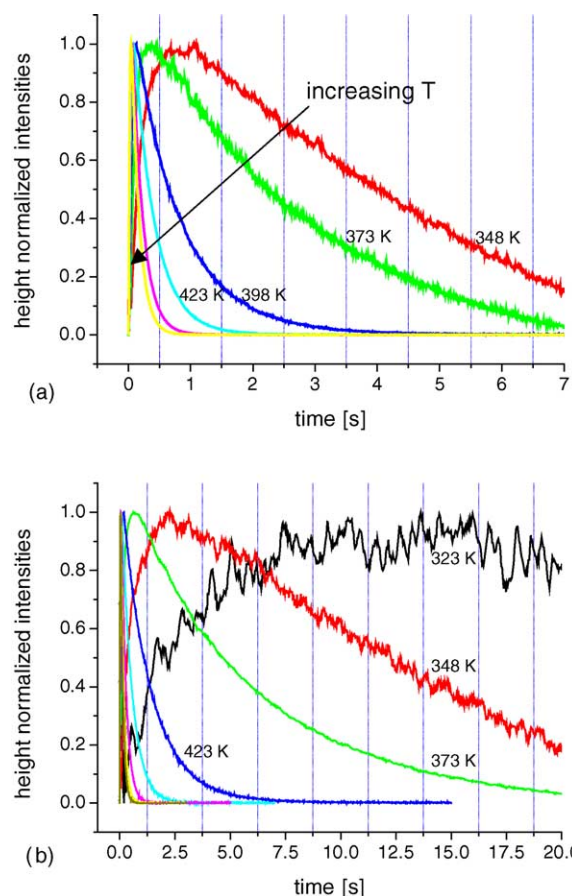


Fig. 5. Height normalized intensities for (a) P1 and (b) C1 at different temperatures.

peratures high residence times were observed corresponding to strong adsorption of *n*-butane with the surface. The residence times decreased with higher temperatures showing less interaction of the probe molecule with the surface. It is interesting to compare the pairs P1/C1 and P2/C2. In both cases *n*-butane was stronger adsorbed on the catalyst material in comparison to the precursor. This is evidently the influence of the surface sulfate groups. Corresponding to this in Fig. 5 the height normalized response curves are given for C1 showing the significant changes of the maxima of the $m/e = 43$ response curves compared to the precursor P1 (C2 changed as well, but not shown here).

The changes in the residence times, going from P1 to C1, were more pronounced than those of the pair P2/C2. As both catalyst samples have the same sulfate contents this points again to the different surface processes (activity) occurring on C1 and C2. The differences were especially strong at low temperature where the highest activity for the isomerization is expected. At higher temperatures (>473 K) however there were no significant differences between the samples, i.e. the residence times reached a constant value for all investigated samples.

To illustrate the influence of porosity and surface activity on the observed response intensities, a nonporous inert ma-

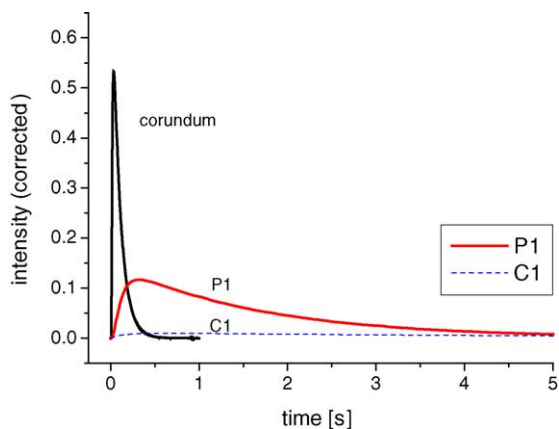


Fig. 6. Response curves for single pulses of *n*-butane over corundum, P1 and C1 at 373 K for $m/e = 43$ (1 g for corundum, 100 mg of sample for P1, C1; inert reference helium) (intensities are corrected to reference helium for corundum).

terial (corundum) was compared with the porous inactive P1 and porous active C1 after pulsing *n*-butane. Fig. 6 shows the changes in the intensities of the response curves for one selected temperature (373 K). All data sets are corrected to the intensity of helium, measured over corundum. Porosity in the sample decreased the intensity due to an increased influence of diffusion processes and also due to adsorption and desorption processes in the inner surface. The intensity of $m/e = 43$ was further lowered for the active material due to the enhanced interaction of the probe molecules with the sulfate groups and by reaction. The differences in these response behaviours of precursor and catalyst will be further investigated and may contribute at least to an estimation of the reaction part in an isomerization reaction within a TAP experiment. Additionally, the knowledge of the influence of porosity on the response curve shape has to be known exactly when experimental outcomes will be used for modelling. It has also to be noted that there may different processes of diffusion (like pore diffusion) take place in porous solids besides the Knudsen diffusion here. As our pore system consisted of mesopores only, an influence of pore diffusion on the experimental outcome could not be observed here. All normalized response curves showed only Knudsen behaviour as described in Section 2.

3.3. TAP—interaction with *iso*-butane

In case of reaction *iso*-butane was formed and had to be desorbed from the surface of the sulfated zirconia as well as the not converted *n*-butane. Therefore, in a next step it was investigated the interaction of the isomerization product *iso*-butane with the porous active and inactive samples. The calculated residence times are listed in Table 4. Two effects can be observed. First, for all temperatures the interaction times of *iso*-butane with surfaces of unsulfated and sulfated zirconia was significantly short-

Table 4

Residence times (s) for pulses of *iso*-butane for P1 and P2, C1 and C2 calculated from the first moments of the response curves, inert reference gases in brackets

Sample (K)	P1 (He)	P2 (He)	C1 (He)	C2 (He)
323	3.2	7.6	7.8	13.5
348	2.4	4.3	5.5	7.0
373	1.7	1.4	1.7	2.5
398	0.69	0.62	0.65	0.73
423	0.36	0.34	0.31	0.39
448	0.20	0.22	–	0.22
473	0.14	0.17	0.14	0.16
498	0.12	0.15	0.11	0.13
523	–	–	0.10	0.11

ened compared to those of *n*-butane. Second, an important difference was found when comparing the pairs P1/C1 and P2/C2. *Iso*-butane showed higher residence times for the pair P2/C2, which was the opposite behaviour compared to that of *n*-butane.

In Fig. 7, the response curves of $m/e = 43$ for three selected temperatures (373, 398, and 423 K) for C1 and C2 are compared, which represent the most interesting temperature interval. For this comparison it was necessary to adjust slightly different overall intensities measured on different days by the MS taking the argon reference gas response of C1 as 100% and correct the responses of C2 to this value. As no conversion of *iso*- to *n*-butane must be assumed due to thermodynamics, the $m/e = 43$ response should be in contrast to the *n*-butane case unique for the probe molecule *iso*-butane. Therefore, the higher intensities observed for C2 can be attributed to a decreased adsorption of *iso*-butane on C2. C1 clearly adsorbed more *iso*-butane than C2, thus the response intensities were lower for C1 than for C2. These results correlate with results from microcalorimetry [11] on this system. Also other groups reported differences in *n*-butane and *iso*-butane adsorption for SZ. Gonzalez et al. described two SZ samples, where similar adsorption of *n*-butane was observed while *iso*-butane adsorption differed for those two samples [15].

As can be seen in Fig. 7 the response curves at one temperature showed the same shape for both samples. This is in contrast to the *n*-butane interaction where the shape of the curves was slightly different (not shown) and this again excludes any contribution of reaction to the shape of the response curve for the *iso*-butane responses. With increasing temperature the shape of the curves was narrowed, too. However, there were observed higher residence times for the pair P2/C2. If C2 adsorbed less *iso*-butane, as could be shown from the intensity profiles, the only explanation for this behaviour is the higher surface area of the samples P2/C2 compared to P1/C1.

The comparison of the nonporous and porous materials for pulsing *iso*-butane is shown in Fig. 8. The differences in the observed overall intensity between P1 and C1 were much smaller compared to that for *n*-butane also indicating that there is no influence of reaction here.

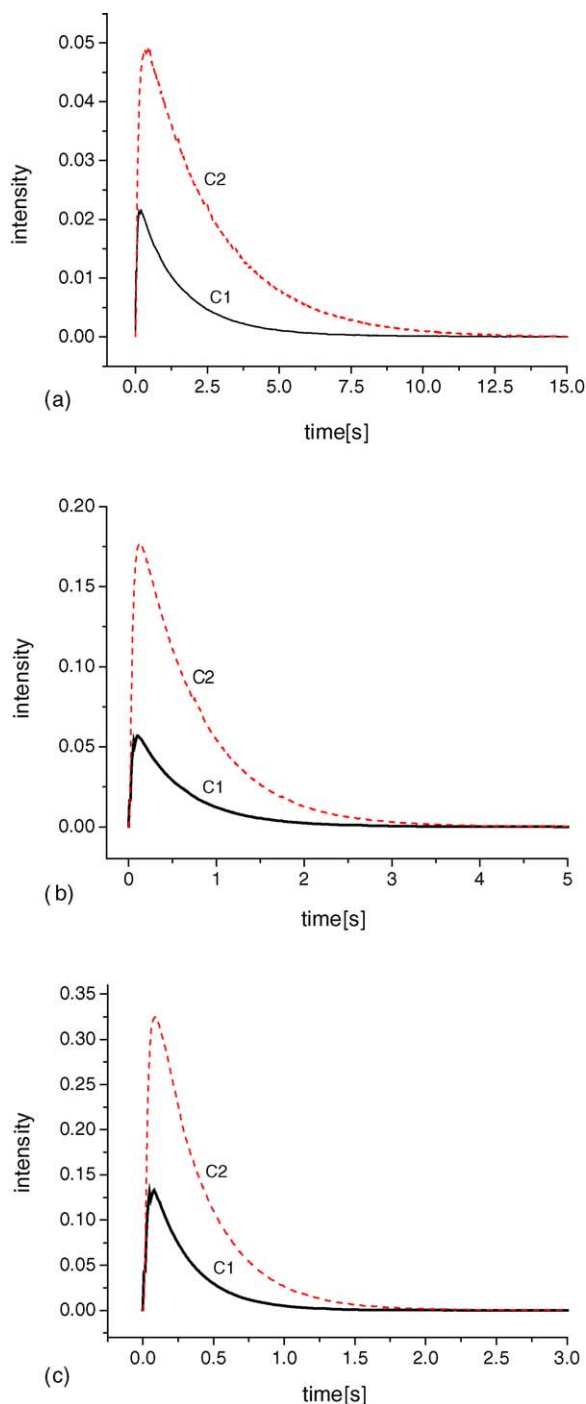


Fig. 7. Corrected intensities of $m/e = 43$ (*iso*-butane) for C1 and C2 at different temperatures (a) 373 K, (b) 398 K, and (c) 423 K.

3.4. Interaction with 1-butene

1-Butene is assumed to be a possible reaction intermediate, side product or deactivating reactant of the isomerization reaction. Therefore, the role of surface sulfate groups for the binding of 1-butene was investigated by pulsing 1-butene. Table 5 shows the calculated residence times for 1-butene over porous inactive and porous active samples.

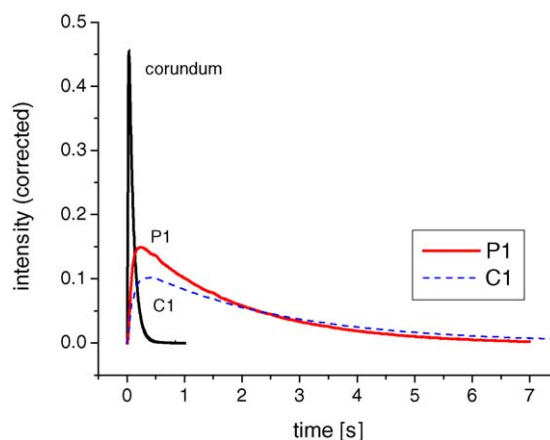


Fig. 8. Response curves for single pulses of *iso*-butane over corundum, P1 and C1 at 373 K $m/e = 43$ (1 g for corundum, 100 mg of sample for P1, C1; inert reference helium) (intensities are corrected to reference helium for corundum).

The adsorptive interaction of 1-butene with the surface of zirconia and sulfated zirconia was strong. No responses were detected below 423 K. At these temperatures 1-butene was irreversibly adsorbed. Further experiments are necessary to investigate whether a saturation phenomenon can be observed with an increasing number of pulses, which would give a break through effect. Also the strong adsorption even at 423 K has to be considered when the isomerization reaction is investigated in more detail in that temperature range. The formation of unsaturated side products may not be observable in a TAP experiment.

The interaction of 1-butene differed for the precursors and the catalyst materials. P1 and P2 showed the same trend with temperature and had comparable residence times although both differ in their specific surface areas. Thus, the interaction of 1-butene with a plain zirconia surface was the same for both samples. In comparison to that the interaction of 1-butene with the sulfated zirconias was stronger and even for higher temperatures long residence times (>20 s) were observed. And both catalyst samples differed in their interaction with 1-butene. The observed response intensities after pulsing 1-butene at 473, 498, and 523 K for C1 and C2 were compared (see Fig. 9). The adsorption of 1-butene was much stronger on C2 than on C1. The curve shapes differed drastically for all investigated temperatures. Fig. 9a exhibits especially for C2 the typical response curve shape with a hump [13] for a fast adsorption and long desorption process. The addition

Table 5

Residence times (s) for P1 and P2, C1 and C2, calculated from the first moments of the response curves of 1-butene ($m/e = 41$)

Sample (K)	P1 (He)	P2 (He)	C1 (He)	C2 (He)
423	3.3	3.4	–	–
448	2.5	2.4	10	13
473	2.2	2.0	6.9	14
498	1.8	1.9	4.3	7.8
523	0.9	1.2	2.2	4.4

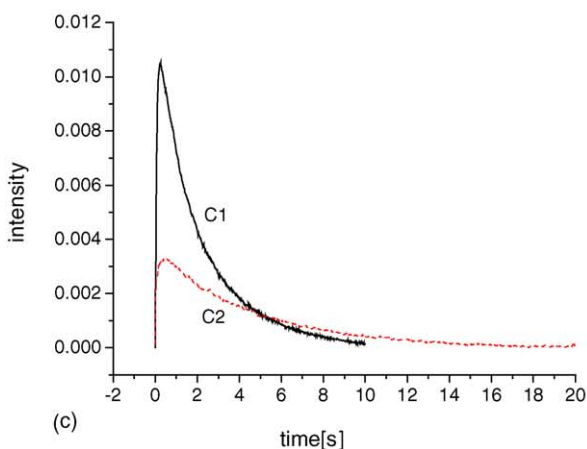
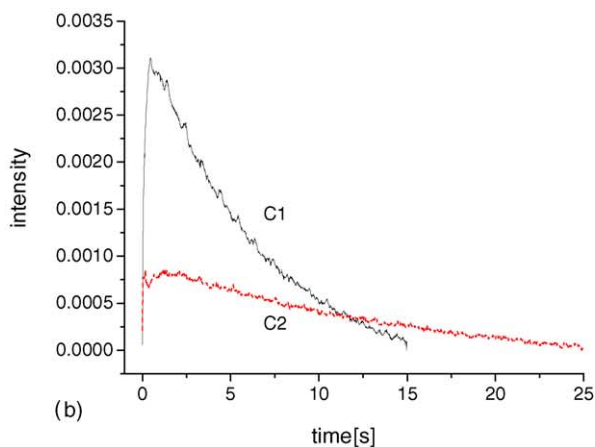
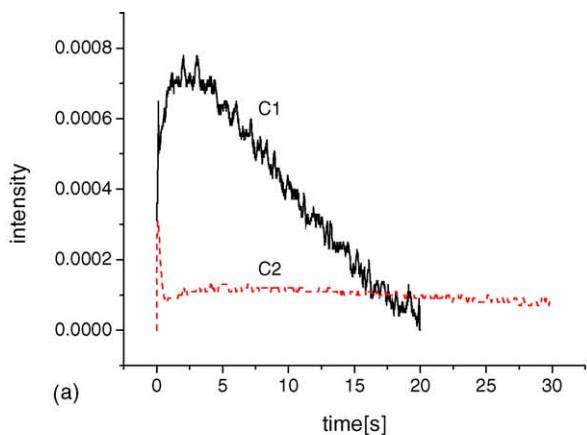


Fig. 9. Corrected intensities of $m/e = 41$ for C1 and C2 at different temperatures (a) 473 K, (b) 498 K, and (c) 523 K.

of sulfate groups enhanced the interaction of 1-butene with the surface and the effect of the different surface area, which increases the residence times, comes into play here.

The different response curves of 1-butene for the non-porous and porous samples (at 473 K) are shown in Fig. 10. 1-Butene is a strongly adsorbing agent on the surface of sulfated zirconia and compared to a nonporous solid also diffusion was much more hindered compared to *n*-butane and *iso*-butane.

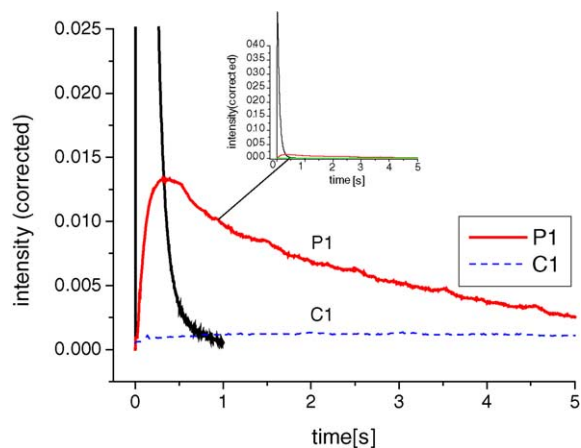


Fig. 10. Response curves for single pulses of 1-butene over corundum, P1 and C1 at 473 K $m/e = 41$ (100 mg of sample for P1, C1, inert reference helium) (intensities are corrected to reference helium for corundum).

It has to be noted that pulsing of 1-butene directly on the surface may differ from a situation in the catalytic cycle, where it may be formed as side product within the reaction sequence. No comparable data are available to address this question. However, the basic adsorption behaviour of 1-butene should be reflected by these experiments.

3.5. Modelling—heats of adsorption

The response curves for pulsing *n*-butane and *iso*-butane, measured at different temperatures, were used to model the adsorption and desorption rate constants on the basis of a simple first order Langmuir adsorption model without assuming reaction. Reaction was excluded in these first attempts of modelling, because the primary aim was to concentrate on adsorption and desorption, only. The modelled curves reproduced the measured response curves quite well. For low temperatures (below 373 K) the modelled curves deviated slightly from the measured ones. This effect has to be investigated in more detail in the future. It is known that Langmuir adsorption may not be adequate if strong site heterogeneity exists [4]. Also a contribution from reaction may lead to this slight deviation. Despite this the basic trends of the modelling was not affected at all. Now kinetic parameters can be extracted out of the fit and the rate constants for adsorption and desorption and their ratios were derived. As long as the underlying model does not contain precise values for a special catalyst (i.e. number of adsorption sites or surface area) the single calculated rate constants are not of physical meaning. The ratio of both rate constants gives us however the estimate for the equilibrium constant.

The heats of adsorption from van't Hoff plots were calculated then for C1 and C2. For the catalytically active C1 a heat of adsorption of 53 kJ/mol was obtained as slope of the linear fit (see Fig. 11). For the inactive sample C2 a quite similar heat of adsorption of 52 kJ/mol was calculated. These values are in very good agreement with calorimetry data [11,15].

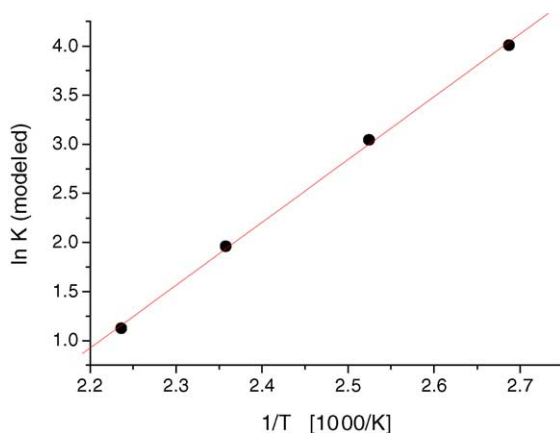


Fig. 11. van't Hoff-plot for *n*-butane over C1 (● modelled values, linear fit).

Thus both catalysts exhibited the same heat of adsorption for *n*-butane. These values are not influenced by a change of the actual catalyst coverage because single pulse experiments are state-defining and should represent the heat of adsorption at low coverages.

However, in comparison to *n*-butane the heats of adsorption for *iso*-butane on active C1 and inactive C2 were more different. The calculated heat of adsorption for *iso*-butane on C1 was 48 kJ/mol, whereas for C2 it was 55 kJ/mol. This again coincided with findings from calorimetry measurements on these two samples cited above.

These experimental and modelling findings can be discussed as follows. The adsorption of *n*-butane on the surface of SZ was similar for the reactive and the nonreactive sample here and seems to be determined only by the overall sulfate content, which is quite similar for the two investigated samples here. Also this seems to be independent from the density of the sulfate groups on the surface of SZ, which was in very good agreement with calorimetry data on this special material [11]. These calorimetry measurements revealed that the majority of sites on the two catalysts were similar.

The heats of adsorption of *iso*-butane differed more for the active and the nonactive samples. Nevertheless, the differences between the samples were small and the catalytic activity may not be accounted on this behaviour alone. However, product adsorption and desorption seems to influence the catalytic activity.

The finding that the adsorption step is so well reproduced by the existing model will be the basis for further modelling on this system which will include a detailed reaction part.

4. Conclusions

Transient measurements with the TAP reactor were performed for the first time to characterize the sorption behaviour of C4-hydrocarbons over sulfated zirconias of different catalytic activity.

It could be shown that the adsorption of the reactant *n*-butane is similar on the catalytically active or inactive sulfated zirconias. The TAP pulse experiments showed that especially at low temperatures there was a strong adsorption of the reactant with extreme long desorption times. The whole process of adsorption was reversible as can be seen from the shape of the TAP pulse responses. These performed TAP experiments refer to a nearly unchanged catalyst surface. Further TAP experiments should be performed on definitely altered surfaces of zirconia to be able to describe the process of activation and deactivation more precisely.

The results obtained on the inactive precursor materials showed that also the unsulfated zirconia surface adsorbed hydrocarbons to a certain amount. This may also influence the measured adsorption on the sulfated zirconias which are not totally covered by sulfate.

The product *iso*-butane showed different adsorption behaviour on catalytically active or inactive material. The adsorption on the partially sulfate covered zirconia, which was catalytically inactive, was less pronounced than on the zirconia with a monolayer sulfate coverage.

Temperature dependent measurements allowed the estimation of heats of adsorption for *n*- and *iso*-butane from transient experiments and revealed comparable heats of adsorption as from calorimetry experiments. These findings will be used to extend the adsorption and desorption model with an appropriate reaction part. The correlation between TAP and calorimetry is also very important regarding the transferability of data from different investigation techniques to bridge the existing pressure gap.

Acknowledgements

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