Ethene Transformation on HZSM-5 studied by Combined UV–VIS Spectroscopy and On-line Gas Chromatography

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Combined UV–VIS spectroscopy in transmission mode and on-line gas chromatography have been performed on a HZSM-5 zeolite in a microreactor operating under a continuous gas flow of either 2 or 20 cm³ min⁻¹ with a mixture of 5 vol.% ethene in nitrogen. The UV–VIS experiments were carried out *in situ* up to 573 K and *ex situ* up to 673 K. Carbocations formed at temperatures up to 473 K are of the cyclopentenyl and/or cyclohexenyl type. Their absorption maxima are between 278 and 313 nm. Moreover, a strong adsorption–sorption is initially established at room temperature which then decreases with time. No appreciable spectroscopic difference could be ascertained between *in situ* and *ex situ* measurements up to 473 K. At 548 K and above the most intense absorption maximum is slightly blue shifted.

The first volatile reaction products could be identified at lower space velocity at ≥ 373 K and aromatics were detected from 573 K. The conversion is strongly dependent on the space velocity. At 523 K and above new absorption bands develop at *ca*. 375 and 440 nm. The former disappears above 573 K and the latter shifts towards 417 nm with increasing temperature. From the location of these bands and from reference experiments we can conclude that for toluene the alkyl-transfer mechanism seems to be valid between 523 and 573 K, and the benzylic-cation mechanism between 573 K.

Catalytic investigations of ethene on zeolites continue to be of interest. This is primarily because the reaction steps for the transformation of ethene first into the carbocations, then into dimers and then into aromatics have not yet been fully explained. In clarifying the question of which intermediates are formed, it can be helpful if catalytic conditions are used. EPR, NMR, TPD and IR have been commonly used in catalytic investigations. In a few cases, UV-VIS spectroscopy¹⁻¹³ has been used, usually in the reflection mode.^{1-7,9,11,13} There are a few studies on ethene-zeolites^{3,4} using UV-VIS in reflection mode; investigations in the transmission mode have only been performed by Karge's group.¹²

For a more comprehensive understanding of the complex reaction sequence one must determine what additional information may be expected from *in situ* measurements, beyond that provided by the *ex situ* measurements, and at which catalyst temperature the first reaction products can be established with an on-line gas chromatograph.

The aims of this work are thus: (i) to create the experimental conditions under which *in situ* UV-VIS spectroscopy in transmission mode can be carried out on the system ethene on an HZSM-5 zeolite up to 573 K; (ii) to undertake *ex situ* UV-VIS spectroscopy in transmission mode and (iii) to use gas chromatographic investigations in order to identify the volatile species formed.

Experimental

The HZSM-5 zeolite (DEGUSSA, CAZ 49) powders, pressed into self-supporting wafers with a weight of 4.5-11.5 mg per cm², were placed in a frame of stainless-steel foil and inserted into a quartz microreactor cell. The cell was connected to a turbomolecular pump-dosing system and to a gas chromatograph.

A Messer-Griesheim pure-grade gas mixture of 5 vol.% ethene in nitrogen was applied. Toluene (Merck, 99.5%), mxylene (Merck, 98%), 1,2,4-trimethylbenzene (1,2,4-TMB) (Fluka, >99.5%) and diphenylmethane (DPM) (Merck, 98%) were used without further purification.

UV-VIS

UV-VIS measurements between 190 and 800 nm in transmission mode were run with a Perkin-Elmer Lambda 9 spectrometer equipped with a scattered transmission accessory installed in the sample compartment as shown in Fig. 1. The accessory was necessary to reduce the influence of radiation scattering in the zeolite samples. The glass reactor cell was constructed in such a way that the optical path from the



Fig. 1 Schematic representation of scattered transmission accessory and reactor cell in the sample compartment of Lambda 9. (1) sample beam; (2) reference beam; (3) catalyst sample; (4) mirrors; (5) heating wire; (6) thermocouple; (7) inlet and outlet for gaseous reactants; (8) inlet and outlet for cooling liquid (water); (9) attenuator; (10) free volume of reactor, ca. 45 cm³; (11) end-on photomultiplier; (12) quartz glass windows (suprasil W)

sample to an end-on photomultiplier placed directly in front of it was only 28 mm. Forward-scattered radiation thus falls almost completely onto the photomultiplier and is included in the measurements. A small quartz glass cooling cell with circulating water was used to thermally isolate the detector from the hot reaction.

With the help of attenuators (1.7 and 10%) the *in situ* measurements could be carried out at up to 573 K (in a few cases up to 623 K). *Ex situ* measurements were performed using the 10% attenuator. All measurements were repeated four to six times and averaged.

The following spectroscopic parameters applied to all measurements: response 0.5 s, slit 5.0 nm, and scan speed 60 nm min⁻¹. Samples were activated *in situ* for 6 h at 723 K *in vacuo* (*ca.* 10^{-5} Pa) in the quartz reactor cell and *in situ* UV-VIS measurements were conducted to obtain background correction data.

Gas Chromatography (GC)

The reactions were carried out in the microreactor operating under a continuous gas flow of either 2 or 20 cm³ min⁻¹ gas mixture. Conversions were monitored and hydrocarbons analysed on line by a Perkin-Elmer gas chromatograph (model 8700) equipped with an automatic heated gas sampling valve and two columns: a 12.5 m plot fused Silica column with 0.53 mm and a bentone 34 + di-n-decyl phthalate column.

Measuring Procedure

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40

20

consumption (%)

In most cases the samples were heated successively from room temperature to 673 K, whereby the time on stream of each adjusted temperature was left between 15 min and a few h. Measurements were then conducted at the raised temperature and after cooling the sample to room temperature. In a few cases the particular sample was brought to a desired temperature and repeated measurements were performed at this temperature as a function of the time on stream.

Results

At first the consumption of ethene on CAZ 49 is relatively large at room temperature and decreases with time until a steady state is reached. This steady state is dependent on the space velocity. For this reason various experimental runs were made at different temperatures varying the WHSV from 0.53 to 16.4 h⁻¹. With high WHSV a faster decrease of the conversion with the time on stream is observed than with lower WHSV (Fig. 2). A decrease in the conversion results

10

time on stream/h

15

20

5



Fig. 3 Conversion of ethene on CAZ 49 with varying catalyst temperature. [], after introduction of ethene; \bigcirc , introduction of ethene after evacuation at room temperature; \triangle , introduction of ethene after evacuation at 673 K for 3 h; \diamond , 2 h evacuated at 673 K, then 2 h exposed to He, subsequently evacuated at room temperature, followed by the introduction of ethene; +, repeated measurement as \diamond after 9 h ethene flux continuous measurement at the different temperature after the + and Y measurement. 20 cm³ min⁻¹ ethene, 5 vol.% in nitrogen; catalyst weight: 5.8 mg per cm⁻², WHSV: 13.0 h⁻¹, time on stream: [], 0.5–2.3 h; \bigcirc , 1.0–2.9 h, \triangle , 0.6–1.7 h; \diamond , 2.4–6.9 h; +, 0.4–2.3 h; X, 0.1–3.9 h; \Leftrightarrow , 1.3–2.8 h; X, 0.1–4.6 h; Z, 2.2–9.2 h; catalyst weight: 5.6 mg per cm⁻², WHSV: 13.5 h⁻¹, time on stream: Y, 0.4–4.0 h; ×, 1.0–4.2 h; *, 0.3–3.9 h; \bowtie , 0.1–1.9 h; \diamondsuit , 0.4–6.0 h; , 0.9–3.3 h

from increasing the reaction temperature going through a maximum at 373 K with a WHSV of *ca.* 13 h⁻¹. The conversion decreases only to 523 K and then increases (Fig. 3). Throughout these experiments the time on stream was always interrupted when the steady state was attained. Furthermore, it is obvious that, in the temperature range investigated, 473–673 K, a linear correlation between the conversion and the WHSV can be drawn (Fig. 4). In these cases the time on stream was selected to be 15 min (WHSV > 2 h⁻¹) and 30 min (WHSV < 2 h⁻¹).

First volatile products such as 2-methylpentene and isobutene could be identified by GC at a WHSV of 1.33 h^{-1} at 373 K. At 473 K a distinctly larger amount of C₃ compounds is found compared to C₄-C₇ compounds (Table 1). The conversion to C₃ compounds decreases with rising temperature while the conversion to C₅ compounds initially increases with temperature and then drops. Also, the conversion to C₆ and C₇ compounds decreases with rising temperature. Benzene, toluene and *p*-xylene are formed only at 573 K and above. Among the xylene isomers the conversion

(d)60 (C) conversion (%) 40 (b) 20 (a) 8 12 14 10 2 4 6 WHSV/h⁻¹

Fig. 4 Conversion of ethene on CAZ 49 vs. the WHSV. 2 and 20 cm³ min⁻¹ ethene, 5 vol.% in nitrogen; time on stream: 15 min (WHSV > 2 h⁻¹), 30 min (WHSV < 2 h⁻¹) (a) 473, (b) 573, (c) 623 and (d) 673 K

Table 1 Conversion and selectivities of ethene on CAZ 49 at different catalyst temperatures

		selectivity (%)										
T/K	conversion (%)	C ₃	$\sum C_4$	$\sum C_5$	$\sum C_6$	$\sum C_{7}$	benzene	toluene	p-xylene	<i>m</i> -xylene	o-xylene	other products
473	6.7	42.0	23.2	17.4	10.1	4.3			_		_	2.9
523	14.1	27.5	31.0	21.8	11.3	6.3	_					2.1
573	41.1	20.7	36.6	21.5	8.0	5.9	1.2	0.7	0.2	2.4		2.7
623	53.5	24.1	37.3	18.7	7.1	5.4	1.3	1.5	0.6	1.5	0.2	2.4
673	76.7	23.6	33.3	10.7	4.8	2.7	0.5	6.0	1.2	6.4	1.0	9.7

 $2 \text{ cm}^3 \text{ min}^{-1}$ ethene, 5 vol.% in N₂; WHSV 1.33 h⁻¹; time on stream 15 min.

to *m*-xylene is the largest. At 673 K a clear increase of conversion to other compounds is observed, as well as to most of those mentioned above and listed in Table 1. At higher space velocities, *e.g.* 13.3 h^{-1} , the first reaction products are only measurable by GC at 473 K and above. In contrast to lower space velocities the selectivity towards C_3-C_6 compounds decreases with temperature increase from 473 to 673 K.

An absorption maximum is detected in the UV-VIS spectra in the range 800-ca. 400 nm at room temperature in the time between filling the reactor cell with nitrogen-ethene and recording the spectra. Its position is dependent on the thickness of the zeolite sample. The thicker the zeolite sample, the further the band of absorption maximum is shifted to higher wavelengths (from 278 to 313 nm) (Table 2 and Fig. 5). In addition, an increase in the intensity of the absorption band is observed with increasing thickness of the sample. No difference could be established either in the intensity of the bands or in the position of the absorption maximum with the use of different gas flow rates. Moreover, a shift of the most intense band with variation in the time on stream could not be detected.

Generally, a shift of the position of the absorption maximum to larger wavelengths was observed by raising the temperature to 373 K. The shift was *ca*. 20 nm in the case of low sample thickness, $\ll 20$ nm in the case of samples with greater thicknesses, but no shift was observed for the samples with the greatest thicknesses (Table 2). Here almost no difference between *ex situ* and *in situ* spectroscopic measurements was discovered (Fig. 6). The absorption maximum did not shift when the temperature was raised to 473 K (Fig. 6). At

523 K a shoulder evolves at ca. 375 nm which is better resolved in the *ex situ* measurements than in the *in situ* ones (Table 3 and Fig. 6). This shoulder is more strongly pronounced if the temperature is raised to 573 K. At even higher temperatures it disappears. After the treatment at 573 K a slight shift of the most intense band to lower wavelengths was observed in *ex situ* measurements only.

With both measuring procedures a broad shoulder develops at ca. 440 nm starting at 523 K (Fig. 6 and 7). The larger intensity of this band in the ex situ measurements in comparison to that in the in situ experiments is striking. At the same time higher intensities and broadening are detected in the 300 nm main absorption bands with in situ measurements than with ex situ ones (Fig. 6). At 523 K and above very weak shoulders evolve at ca. 475 nm for samples with a weight of 5.0 mg per cm^2 and more in the ex situ measurements. These shoulders are more clearly pronounced above 573 K, as can be seen from Fig. 7 at 673 K, and they are observable also at this temperature for the samples with the lowest weight (Table 3). An increase in the intensity is observed with the samples up to 10 mg per cm² at 573 to 673 K for the next strongest band. At 673 K this band is comparable in intensity to the one at ca. 310 nm. In addition, one can observe a shift of the 440 nm band to 417 (8) nm for all samples (Table 3). At the 11.5 mg per cm² zeolite sample the intensity of the band at 418 nm is clearly greater than at 313 nm. The shoulder which evolves at 523 K changes into a strong band at 548 K when the time on stream is increased. This band is shifted towards 418 nm also (Fig. 8). In this case it is striking that the shift of the most intense band is more

Table 2 Absorption maxima (nm) at ca. 300 nm of carbocations formed from ethene in CAZ 49 at different temperatures

	sample weight/mg per cm ⁻²								
T/K	4.6	4.7	5.0	5.5	6.6	10.0	11.5		
room temp.	278	272	281	295	302	310	313		
373	300 ⁱⁿ	298 ⁱⁿ	305 ⁱⁿ	304 ⁱⁿ	312 ⁱⁿ	311 ⁱⁿ	314 ⁱⁿ		
	301 ^{ex}	298 ^{ex}	305ex	305ex	312 ^{ex}	311 ^{ex}	307ex		
423	310 ⁱⁿ	308 ⁱⁿ	310 ⁱⁿ	307 ⁱⁿ	313 ⁱⁿ				
	310 ^{ex}	308 ^{ex}	310 ^{ex}	307 ^{ex}	312 ^{ex}	n.m.	n.m.		
473	310 ⁱⁿ	307 ⁱⁿ	310 ⁱⁿ	305 ⁱⁿ	311 ⁱⁿ	312 ⁱⁿ	313 ⁱⁿ		
	310 ^{ex}	305°×	306ex	305 ^{ex}	309 ^{ex}	309ex	312ex		
523	309 ⁱⁿ	312 ⁱⁿ	312 ⁱⁿ		313 ⁱⁿ	315 ⁱⁿ	322 ⁱⁿ		
	310 ^{ex}	311ex	312 ^{ex}	n.m .	314 ^{ex}	312ex	316 ^{ex}		
548	320 ⁱⁿ	312 ⁱⁿ	312 ⁱⁿ	322 ⁱⁿ	314 ⁱⁿ	317 ⁱⁿ			
	305ex	310 ^{ex}	309ex	306 ^{ex}	312ex	311ex	n.m .		
573	311 ⁱⁿ	308 ⁱⁿ	309 ⁱⁿ	*333 ⁱⁿ	311 ⁱⁿ	313 ⁱⁿ	335 ⁱⁿ		
	307ex	304 ^{ex}	306 ^{ex}	306ex	310 ^{ex}	308ex	312 ^{ex}		
598		320 ⁱⁿ		338 ⁱⁿ	*309 ⁱⁿ				
	302ex	303ex	304 ^{ex}	302ex	309ex	n.m.	n.m .		
623				*340 ⁱⁿ					
	302ex	307 ^{ex}	302ex	302ex	308ex	340ex	313ex		
673	303ex	n.m.	302ex	300 ^{ex}	307ex	306 ^{ex}	313ex		

 $20 \text{ cm}^3 \text{ min}^{-1}$ ethene, 5 vol.% in N₂; time on stream 1 h.

* Bands of questionable presence; n.m., not measured.



Fig. 5 UV-VIS difference spectra of ethene adsorbed-sorbed on CAZ 49 at room temperature. 20 cm³ min⁻¹ ethene, 5 vol.% in nitrogen; time on stream: 1 h (a) 5.0, (b) 6.6 and (c) 11.5 mg cm⁻²

clear in ex situ measurements (312 nm after 24 h in situ, 332 nm after 25 h ex situ) than in cases in which time on stream remained constant (Table 2). These investigations were not carried out on zeolite samples of different weights.

Furthermore, new bands appearing as weak shoulders evolve with some CAZ 49 samples between 500 and 510 nm at 573 to 673 K and only in *ex situ* measurements between 590 and 610 nm at 623 K and 673 K [Table 3 and Fig. 7, only a weak shoulder is recognizable here at *ca.* 600 nm (673 K)].

When the temperature is increased to 373 K after a long time on stream, there is still no shift of the most intense band. However, the intensity of the strongest band increases sharply with an ethene-nitrogen flow rate of $2 \text{ cm}^3 \text{ min}^{-1}$ as can be seen in Fig. 9. Following evacuation the most intense

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Fig. 6 UV-VIS electron difference spectra of ethene-loaded CAZ 49 (10.0 mg cm⁻²) 20 cm³ min⁻¹ ethene, 5 vol.% in nitrogen; time on stream: 1 h (a) room temperature; (b) 373; (c) 473; (d) 523 and (e) 573 K; (----) in situ, (----) ex situ

band shifted slightly to a higher wavelength and the intensity decreased.

Discussion

The GC results for the relation of ethene consumption to time on stream at room temperature, initially a strong adsorption-sorption which then gradually decreases over a long time, correspond well with the results of adsorption investigations by other authors.^{14–16} However, in our example with a zeolite sample with low weight (Fig. 2) saturation of the zeolite sample with ethene is attained more quickly (ca. 22 h) than in thermogravimetric experiments (ca. 60 h).^{14–16}

Table 3 Visible spectroscopic data (nm) between 360 and 600 nm for ethene adsorbed-sorbed on CAZ 49 at different temperatures

		sample weight/mg per cm ²								
T/K	4.6	4.7	5.0	5.5	6.6	10.0	11.5			
523	373 ⁱⁿ	364 ⁱⁿ		371 ⁱⁿ	372 ⁱⁿ	373 ⁱⁿ	372 ⁱⁿ			
	376 ^{ex}	368ex	362 ^{ex}	365ex	367ex	368 ^{ex}	364 ^{ex}			
	443 ⁱⁿ	441 ⁱⁿ	442 ⁱⁿ	441 ⁱⁿ	440 ⁱⁿ	440 ⁱⁿ	439 ⁱⁿ			
	440 ^{ex}	440 ^{ex}	441 ^{ex}	439ex	440 ^{ex}	439 ^{ex}	438 ^{ex}			
			*485 ⁱⁿ	*480ex	*479 ^{ex}	*481 ^{ex}	*478 ^{ex}			
							*561ex			
548		*368 ⁱⁿ		*377 ⁱⁿ	*370 ⁱⁿ	*371 ⁱⁿ				
	367ex	372ex	365ex	368ex	368 ^{ex}	366 ^{ex}				
	427 ⁱⁿ	444 ⁱⁿ	434 ⁱⁿ	433 ⁱⁿ	437 ⁱⁿ	434 ⁱⁿ	n.m.			
	423ex	418 ^{ex}	430 ^{ex}	430 ^{ex}	438 ^{ex}	433 ^{ex}				
			*478 ^{ex}	*479 ^{ex}		*478 ^{ex}				
573	*365 ⁱⁿ						428 ⁱⁿ			
	*379ex		*382ex	378 ^{ex}	*378ex	374 ^{ex}	422 ^{ex}			
	420 ⁱⁿ	420 ⁱⁿ	422 ⁱⁿ	424 ⁱⁿ	427 ⁱⁿ	429 ⁱⁿ	*474 ⁱⁿ			
	418 ^{ex}	416 ^{ex}	418 ^{ex}	420 ^{ex}	421 ^{ex}	427 ^{ex}	473 ^{ex}			
		*502ex					*507 ⁱⁿ			
							*503ex			
623				420 ⁱⁿ	420 ⁱⁿ		423 ⁱⁿ			
	416 ^{ex}	418 ^{ex}	417 ^{ex}	418 ^{ex}	419 ^{ex}	421 ^{ex}	418 ^{ex}			
				477 ⁱⁿ	477 ⁱⁿ		473 ⁱⁿ			
	*478°×	*476ex	*478 ^{ex}	*480 ^{ex}	*481 ^{ex}	*477 ^{ex}	479 ^{ex}			
				*510 ⁱⁿ			508 ⁱⁿ			
	*595°x	*594°×			*609ex	*605ex	*602ex			
673	417 ^{ex}		418 ^{ex}	417 ^{ex}	417 ^{ex}	417 ^{ex}	418 ^{ex}			
	*480 ^{ex}	n.m.	478 ^{ex}	479 ^{ex}	479 ^{ex}	483 ^{ex}	477 ^{ex}			
							509ex			
	*600 ^{ex}		*598ex	599 ^{ex}	*601 ^{ex}	*601 ^{ex}	589ex			

 $20 \text{ cm}^3 \text{ min}^{-1}$ ethene, 5 vol.% in N₂; time on stream 1 h.

* Bands of questionable presence or very weak absorptions; n.m., not measured.



Fig. 7 Ex situ UV-VIS electron difference spectra of ethene-loaded CAZ 49 (10.0 mg cm⁻²). 20 cm³ min⁻¹ ethene, 5 vol.% in nitrogen; time on stream: 1 h (a) room temperature, (b) 573, (c) 623 and (d) 673 K

The increase in conversion is primarily due to the formation of volatile reaction products. The decreasing ethene conversion with increasing temperature can be explained by the greater thermal dislocation of the ethene molecules, leaving less space in the narrow pores of the CAZ 49 for the arriving ethene molecules. In addition, the applied temperature is quite high for ethene if one compares it with hydrocarbons with more C atoms.

In contrast to our results the increase of conversion with the WHSV was not as great as for n-butenes conversion on HZSM-5 zeolites with shorter times on stream.¹⁷ One possible reason for this behaviour might be the following: If one considers the contact times of the applied reaction gas then one observes that these are much greater for the smallest WHSV in the present investigations than in the butenes conversions (45 min cf. 15 min). Apparently, much greater conversions of ethene on CAZ 49 can be expected with very high contact times and short times on stream. This assumption is confirmed by the investigation of ethene consumption depending on the time on stream at a WHSV of 0.53 h^{-1} at room temperature (Fig. 2). The dependence of conversion on the time on stream suggests that for small WHSVs ($<2 h^{-1}$) and a complete adsorption-sorption of ethene on CAZ 49, the conversion is lower at higher temperatures than with the use of shorter times on stream at the same WHSVs. However, further experiments are necessary to clarify this.

As is known, carbocations can be formed on acid centres of zeolites under catalytic conditions using hydrocarbons. Our



Fig. 8 In situ UV-VIS difference spectra of ethene adsorbed-sorbed on CAZ 49 (5.6 mg cm⁻²) at 548 K. 20 cm³ min⁻¹ ethene, 5 vol.% in nitrogen; time on stream: (a) 1, (b) 2, (c) 9, (d) 10, (e) 24 and (f) 25 h (ex situ)



Fig. 9 UV-VIS difference spectra of CAZ 49 (5.4 mg cm⁻²) exposed to ethene. 2 cm³ min⁻¹ ethene, 5 vol.% in nitrogen; time on stream: (a) (----) 1 h; (----) 5 h; (----) 15 h and (----) 24 h at room temperature, (b) (-----) 1 h and (-----) 2 h at 373 K (in situ), (c) (-----) 1 h, and 7 h and (-----) 16 h at room temperature (during evacuation)

results allow us to conclude that owing to the different peak positions of the absorption maximum, various monoenylic carbocations are formed at room temperature and 373 K. The peak positions observed point to cyclopentenyl and/or cyclohexenyl carbocations which have been identified in strong acids,^{18,19} but the presence of linear monoenylic carbocations cannot be ruled out.

The dependence of the absorption maximum on the sample weight is not surprising since the number of acid centres increases with increasing sample weight. In a very recent paper by Kirisci *et al.*²⁰ a red shift of the most intense band was also established with increasing ratio of the Brønsted to Lewis acidity at room temperature based on UV–VIS measurements. Moreover, the greater intensity of the absorption bands implies a greater stability of the carbocations formed. This is obvious from the slight shift of the most intense band of the absorption maximum of samples with the greater weight at increasing temperature (Table 2). Since the ratio of the Brønsted to Lewis acidity and probably also the strength of acidity remain constant, the increasing number of Lewisacid centres could be responsible for the increase in the intensity of absorption bands.

The experimental findings concerning the samples with low weights are confirmed by UV-VIS reflection measurements at room temperature in which the absorption maximum at ca. 290 nm is independent of the sample weight because of the same penetrating depth of light into the samples. Moreover, a possible explanation for the dependence of the most intense absorption maximum on the weight of zeolite samples could also be that through the transformation of ethene into carbocations a clearly greater local overheating occurs in the heavier samples. With lighter samples, these carbocations are only formed at higher temperatures.

The protonation of ethene and the hydride transfer²¹ could develop on both the Lewis-acid and Brønsted centres available in the HZSM-5 zeolite. While it has been shown by Berg *et al.*²² that linear oligomers are formed on the strong Brønsted centres after longer contact time at room temperature and branched oligomers at 373 K, the carbocations given above can presumably develop quickly on the Lewisacid centres. If UV-VIS spectra are compared with the spectra of cyclocarbocations yielded in strong acids, one can assume from the spectral width at the base that in each case only one carbocation is represented by the most intense band. Cyclohexenyl carbocations are probably formed with low sample weights at higher temperatures. With large sample weights (10.0 and 11.5 mg per cm²) these carbocations already exist at room temperature. Moreover, the data of Table 2 suggest that cyclohexenyl carbocations with a larger number of alkenyl groups could be produced. Also, it is possible, that the different cyclic carbocations mentioned above exist in various concentrations depending on sample weight and temperature. The shoulder at ca. 375 nm at 523 K and above after treatment may be assigned to cyclohexadienyl carbocations which are produced from cyclohexenyl carbocations on acidic Lewis sites. The reaction equilibrium is probably shifted to the side of cyclohexadienyl carbocations which are formed endothermically because the peak at ca. 375 nm is more clearly seen in the ex situ measurements than in the in situ ones. The disappearance of the band at ca. 375 nm at temperatures higher than 573 K must be attributed to the fact that the corresponding volatile aromatics are formed from the cyclohexadienyl carbocations which we have determined by GC (see Table 1).

Note that a correlation between the intensities of the UV–VIS peaks and the ethene conversions on CAZ 49 at the different catalyst temperatures cannot be found.

The absorption band which emerges at higher temperatures at *ca.* 475 nm may suggest that linear and/or cyclic trienylic carbocations $(\lambda_{max} = 473, 470 \text{ nm})^{18,23}$ are formed although linear and/or cyclic dienylic carbocations $[\lambda_{max} = 397(6), 395 \text{ nm}]^{18,23}$ should also be observed in the UV–VIS spectra. Nevertheless, if one starts from a shift of *ca.* 20 nm towards higher wavelengths, one finds that the peak position of the absorption maximum would correspond to linear and/or cyclic dienylic carbocations formed in strong acids, such as 80–96% H₂SO₄.¹⁸ Polynuclear cyclohexadienyl carbocations can be assigned to the bands which are recognizable as weak shoulders between 500 and 510 nm and between 590 and 610 nm. Polynuclear aromatics which presumably developed from the protonate polynuclear aromatics at higher temperatures (see above) cannot be identified by GC.

One can conclude from the intensity of the most prominent bands of *in situ* measurements that the carbocations formed are very stable. In addition, one observes, for instance in *in situ* measurements at 573 K, broad overlapping bands which are certainly made up of individual bands of several carbocations. A small broadening of the absorption maximum already takes place above 473 K [see Fig. 6(c)] and at 548 K [Fig. 8(e) and (f)]. The clearly discernible discrepancy in the

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position of the absorption maximum between in situ and ex situ measurements above 548 K (Table 2) should presumably be attributed to the formation of carbocations, or to the existence of such carbocations from an equilibrium reaction, which are more stable at room temperature than at higher temperatures. The shift in the most intense bands towards lower wavelengths at higher temperatures (598-673 K) is probably attributable to the decreased proportion of cyclohexenyl carbocations.

Based on the bands with absorption maxima at ca. 375 nm and 440 (417) nm (see Table 3) and the results of others authors we can assume that aromatics (e.g. toluene) on certain zeolites disproportionate at higher temperatures and they thereby transform, in part, into carbocations. In order to clarify this phenomenon some spectroscopic measurements on aromatics, given in the experimental section, were performed as well. From the spectroscopic results of these aromatics obtained from CAZ 49 zeolite samples (Table 4) and the bands which evolved at ca. 375 nm and at 440 (417) nm in the ethene catalysis the following conclusions can be drawn: At 523 K and above toluene is formed and this in turn is probably transformed partly into other compounds on the strong Brønsted centres. This occurs via the alkyl-transfer and benzylic-cation mechanism, as propounded by Gnep and Guisnet.²⁴ According to the former mechanism (see Scheme 1) bands should be found with absorption maxima between 330 and 340 nm at room temperature which can be attributed to methyl- and dimethyl-cyclohexadienyl carbocations

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zeolite	aromatics	T/\mathbf{K}	λ_{max}/nm	ref.
HZSM-5	toluene ^a	298	258 350 453	13
		573-423	460	
CA7 40		208	208 (et) - 258 (et)	this work
CAZ 49		230	200 (st) - 250 (st) $208^{in} (st) - 262^{in} (st) - 370^{in} (st)$	uns work
		572	208 (st) 202 (st) 570 (st) $212^{in} (st) 265^{in} (st) 270^{in} (st) 455^{in} (st)$	
H-mordenite HMD-2	<i>m</i> -xylene ^b	515	(212 (31) 203 (31) 370 (31) 433 (31)	11
H-mordenite HMD-4	m xylone	298	335 483	
CAZ 49		298	194 (st) 255	this work
		373	206^{in} (st) 262^{in} (st) 338^{in} (st)	
		473	210^{in} (st) 272^{in} (sh) 356^{in} (sh) 342^{ex} 442^{in}	
H-mordenite HMD-2 H-mordenite HMD-4	1.2. 4-TMB ^c	298	{ 245 354 355	11
CAZ 49	-,_,	298	210 (st) 268 355	this work
		373	210^{in} (st) 267^{in} (st) 272^{ex} 368^{in}	
		473	212 ⁱⁿ (st) 368 ⁱⁿ (st) 360 ^{ex} 458 ⁱⁿ 452 ^{ex}	
mordenite HM and HZSM-5	DPM^d	298	440	13
CAZ 49		298	218 262	this work
		373	214 ⁱⁿ 268 ⁱⁿ 435 ⁱⁿ (st)	
		423	208 ⁱⁿ 268 ⁱⁿ (st) 298 ⁱⁿ 342 ⁱⁿ 438 ⁱⁿ (st) 445 ^{ex} (st)	
				·

Table 4 Electronic transitions observed upon adsorption-sorption of different adsorbates on HZSM-5 and mordenites

^a 6.4 vol.%; ^b 13.8 vol.%; ^c 46 vol.%; ^d 4.1 vol.%, all in N₂. Ex situ values only given if the difference between in and ex situ λ_{max} was greater than 4 nm. st: strong; sh: shoulder.

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$$\bigcup^{CH_3} + Z^- H^+ \longrightarrow \bigcup^{CH_2^+} Z^- + H_2$$
(1)

$$\bigcup_{Z^-}^{CH_2^+} \bigcup_{Z^-}^{CH_3} \Longrightarrow \bigcup_{Z^-}^{CH_2} \bigcup_{CH_3}^{CH_2}$$
(2)

$$\underbrace{ \begin{array}{c} \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array}$$



developed in strong acids.¹⁸ However, our measurements yield absorption maxima in almost the same position for ethene-CAZ 49 and the investigated toluene-CAZ 49 (Table 3 and 4). These absorption maxima show a red shift of only ca. 20 nm relative to toluene-HZSM-5 measured by Chen et al.13 Aromatics with greater basicity such as m-xylene and 1,2,4-TMB are already transformed into cyclohexadienyl carbocations at low temperatures which is consistent with the results of Naccache et al.¹¹ The absorption maximum for mxylene at 373 K corresponds with that of the dimethylcyclohexadienyl carbocation observed in strong acid medium,¹⁸ whereas a red shift of 13 nm to the protonated species for 1,2,4-TMB at 373 K is also attested. Moreover, a small shift towards larger wavelengths occurs from m-xylene with increasing temperature. Assuming the alkyl-transfer mechanism is correct, m-xylene should be formed. Indeed, we could identify m-xylene in low amounts by GC for the system toluene-CAZ 49. For the above reasons it seems clear that toluene disproportionation takes place according to the alkyl-transfer mechanism in the temperature range 523-573 K

On the other hand, as has already been mentioned, the benzylic-cation mechanism (see Scheme 2) applies to our results as well. Because the benzyl carbocations formed according to this mechanism can evidently only be observed spectroscopically at low temperatures (e.g. 223 K), they cannot be detected in our UV-VIS spectra. Instead, the formation of a diphenylmethylcarbonium ion intermediary is observed. According to Scheme 2, the peak of such an ion with a methyl group in the para position would presumably be located somewhat above 440 nm as we observed and as did other authors (Table 4). The absorption peak at 440 nm at increasing temperatures shows a blue shift. This can be explained by the fact that for a disproportionation according to Scheme 2 other aromatics can be expected as well. Thus, e.g. the 1,1-diphenylpropylcarbonium ion, measured in acid medium and showing an absorption maximum of 422 nm,¹⁸ might be developed according to the reaction pathway (4b) (see Scheme 2).¹³ This assumes that the diphenylcarbonium ion above 523 K reacts with propene most probably formed during the catalysis. Such a carbonium ion could contribute to the above mentioned blue shift. Here, the crack products of the transformation of the $C_6H_5CH_2C_6H_5CH_3$ cation into benzene and xylenes [see reaction pathways (4a) and (4b) of Scheme 2] were identified by GC in small amounts from 523 K. In conclusion, it can also be established that both reaction mechanisms mentioned are in operation at temperatures above 523 K. Moreover, it is shown that the disproportionation of aromatic hydrocarbons only takes place through the benzylic-cation mechanism in the temperature range 573-673 K.

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