

Sorption and Catalytic Reaction in Pentasil Zeolites. Influence of Preparation and Crystal Size on Equilibria and Kinetics

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Zeolite ZSM-5 was synthesized in the H form by two different methods. The product from one of these preparations was separated into fractions of different crystal size. Sorption equilibria, rates of sorption and desorption, and rates of catalytic conversion of methanol, dimethyl ether, and various hydrocarbons were investigated with these materials. Mainly sorption rates but also catalytic properties depend on the method of preparation of the zeolite. Product distribution in catalytic reactions is furthermore influenced by intercrystalline mass transfer (pellet geometry), but it is independent of crystal size for dimethyl ether or propene as starting materials. For dimethyl ether as reactant the intracrystalline Thiele number was found to be smaller than unity in crystals of 0.5 μm diameter.

Synthetic silica-rich protectosilicates known as Zeolites Socony-Mobil 5 and 11 (ZSM 5 and ZSM 11 for short) have been of considerable interest since it was announced that these materials are suitable catalysts for the conversion of methanol to olefins and to hydrocarbons in the gasoline range (1) as well as for the alkylation of aromatic hydrocarbons (2), exhibiting a rather high thermal stability and a low rate of deactivation. The global kinetics of the consecutive reactions from methanol via dimethyl ether to hydrocarbons on zeolite ZSM 5 have been described by Chang and Silvestri (3), Chang *et al.* (4), and by Anderson and co-workers (5); the mechanism of these reactions has recently been debated in several publications (6-9). The crystal structures of zeolites ZSM 5 and ZSM 11 which have been determined by Kokotailo *et al.* (10) and Kokotailo and Meier (11) are closely related and it appears that silicon can be substituted for aluminum

without affecting the basic structure until the lattice consists of pure SiO_2 (12). The generic name "Pentasil" was therefore proposed by Kokotailo and Meier (11) to designate these solids, irrespective of minor differences in crystal structure or composition and of the method of preparation.

Many commercial catalysts are thermodynamically metastable solids (as are these zeolites) and their catalytic properties depend frequently in a rather subtle way on the method of preparation, as well as on composition and crystal structure as determined by X-ray diffraction. It was therefore one object of the present work to find out what influence the preparation method might have on the catalytic properties and sorption behaviour of Pentasil zeolites.

Furthermore, we intended to investigate the following questions:

(a) To what degree are the reactions of methanol, dimethyl ether, and hydrocarbons in these zeolites limited to regions

near the crystal surface, due to a limited rate of diffusion of reactants in the channels of the structure?

(b) What is the relative influence of consecutive reactions of primary gaseous products on the product spectrum or selectivity of the reaction network?

With respect to these questions the rates of sorption and of reaction of different starting materials (methanol, ether, hydrocarbons) had to be obtained for the same zeolite preparations and the influence of the crystal size on these rate phenomena was also investigated.

NOMENCLATURE

D	diffusion coefficient
ΔH_S	differential heat of sorption
k_1, k_2	rate constants
m_z	mass of zeolite sample
m_s	mass of sorbate
n, n_0, n_t	sorbed amount at $t, t = 0, t \rightarrow \infty$
$\frac{\Delta n}{\Delta n_t}$	$\frac{n - n_0}{n_t - n_0}$
\dot{n}_i	moles produced or moles reacted of species i per second
p	pressure
p_t	equilibrium pressure
p_{sat}	saturation pressure at 293 K
\bar{p}	pressure of reactant in the differential reactor
r	rate of reaction
R	radius of single crystals
\bar{r}	radius of single pellets
T	temperature
t	time
V_z	crystal volume

EXPERIMENTAL

Zeolite Materials

Zeolite ZSM 5 in the hydrogen form was prepared by two procedures. The first method consisted in crystallizing at 408 K the Na form from a gel containing tetrapropylammonium ion as organic base, as described by Argauer and Landolt (13) in the original patent. The Na form was subse-

quently exchanged three times with 1 M NH_4Cl solution, the resulting NH_4 -zeolite then being heated for 3 h at 923 K to obtain the H form, designated here as "Pentasil I." A different method for obtaining a zeolite with the same structure exhibiting an identical X-ray diffraction pattern has been

TABLE 1
Properties of Zeolite Preparations

	Pentasil			
	I	II	III	
$\text{SiO}_2/\text{Al}_2\text{O}_3$ (mol):	65	130	34	
(surface):	(97)	(140)	(96)	
Crystal diameter (μm):	2 ± 0.5	0.5 ± 0.1	14 ± 2	
Residual Na content (wt%):	<0.2	<0.2	<0.2	
Equil. sorption of n -hexane at 293 K and $p = 0.133$ mbar (mol/g dry zeol.):	2.73×10^{-4}	1.28×10^{-3}	8.41×10^{-4}	
	Pentasil I		Pentasil II + III	
	d	$I/I' \cdot 100$	d	$I/I' \cdot 100$
	11.112	92	11.112	71
	10.010	82	9.980	90
	9.761	7	9.755	7
	6.691	9	6.720	11
	6.342	15	6.349	4
	5.982	24	5.970	24
	5.690	13	5.694	6
	5.554	15	5.564	11
	5.376	4		
	4.989	8	5.008	9
	4.604	8	4.618	5
	4.350	12	4.352	7
	4.260	13	4.268	5
	4.005	8	4.008	3
	3.850	100	3.844	100
	3.825	77	3.810	73
	3.744	43	3.743	22
	3.713	49	3.713	34
	3.641	25	3.644	10
			3.592	5
	3.450	9	3.462	5
	3.335	8	3.341	6
	3.298	9	3.310	6
	3.247	6		
	3.048	8	3.048	10
	2.985	15	2.983	11
	2.864	4	2.864	3
	2.734	4		
	2.609	4	2.603	4
	2.513	4	2.513	3
	2.489	6	2.488	4
	2.406	4	2.411	3
	2.397	4	2.392	3
	2.012	9	2.007	9
	1.994	9	1.991	8

Note. Lattice parameter d in Angström units (10^{-10} m) and relative intensities $I/I' \cdot 100$ of corresponding X-ray reflections.

described in a German patent (14), crystals being formed with 1,6-diaminohexane as organic base from a sodium-free gel, which after heating in air at 823 K yield immediately the hydrogen form without an intermediate ion exchange. The material obtained in this way is designated here as "Pentasil II" (crystal size, $0.5 \pm 0.1 \mu\text{m}$) and "Pentasil III" (crystal size, $14 \pm 2 \mu\text{m}$); different size fractions were separated by air classification and dry sieving.

Properties of all three materials are listed in Table 1; the $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratios have been obtained by wet chemical analysis characterizing the bulk composition of the solid. In addition, the $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratio near the surface of the crystals was determined by energy-dispersive X-ray fluorescence in an approximate way, and these values are shown in parentheses; they indicate that the surface-near regions are deficient in aluminum, which explains why different $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratios are obtained for the bulk of smaller crystals as compared to large crystals from the same batch. The Guinier X-ray powder diffraction (XRD) patterns of small and large crystals from this Na-free preparation (samples II and III, respectively) were identical. Figure 1 shows the intensities of XRD of Pentasil I and of a mixture of Pentasil II + III. Lattice spacings d and relative intensities of corresponding reflections are also given in Table 1. There are only minor variations in the diffraction patterns of the materials synthesized by the two different methods, these patterns corresponding to specifications for zeolite ZSM 5 (13) in both cases.

Procedure for Sorption and Catalysis Studies

Equilibria and rates of sorption were obtained by the gravimetric method as described in previous publications (15, 16), where it has been emphasized that external and intracrystalline mass transfer, as well as heat transfer, have to be considered in the interpretation of rates of sorption or desorption. This point has also been elabo-

rated on recently by Kärger (17) and by Ruthven and co-workers (18, 19). For each sorbate-sorbent system the zeolite sample was degassed at 623 K for 3 h at $p \leq 1.33 \times 10^{-6}$ bar. Sorbate was then admitted at the specified temperature in a stepwise fashion (increasing equilibrium pressure) and the procedure reversed at stepwise decreasing pressure, an equilibrium isotherm being defined by the coincidence of points obtained in sorption and desorption. The kinetics of equilibration of the system were recorded for each sorption or desorption step.

Rates of catalytic reactions were observed in a fixed-bed reactor operated in the differential mode, conversion of reactants being below 20% at a gas flow rate of $13 \text{ cm}^3/\text{sec}$ (298 K, 1 bar). The reactor consisted of an externally heated glass tube (i.d. 10 mm) containing in each case 0.27 g of catalyst in the form of loosely pressed pellets of different sizes, diluted with glass beads. It was operated at atmospheric pressure, the controlled flow of reactants (3.3 mol% in He) entering the reactor after passing a preheating zone. Reaction temperature was determined with a thermocouple located in the upper part of the catalyst bed. The reaction mixture was analyzed by temperature-programmed capillary gas chromatography (100-m OV 101, i.d. = 0.3 mm). Before each run the catalyst was heated in air at a rate of 4 K/min to 923 K and then cooled to reaction temperature; rate measurements were obtained after a constant flow of reactant in He had passed over the catalyst at reaction temperature for 2 h in each case. After an initial minor decrease in activity the observed rate of reaction did not decrease by more than 5% between 2 and 10 h on-stream time of the catalyst.

RESULTS

(a) Reversible Sorption

Sorption of methanol, dimethyl ether, paraffinic hydrocarbons, and benzene was found to be reversible in all three zeolite

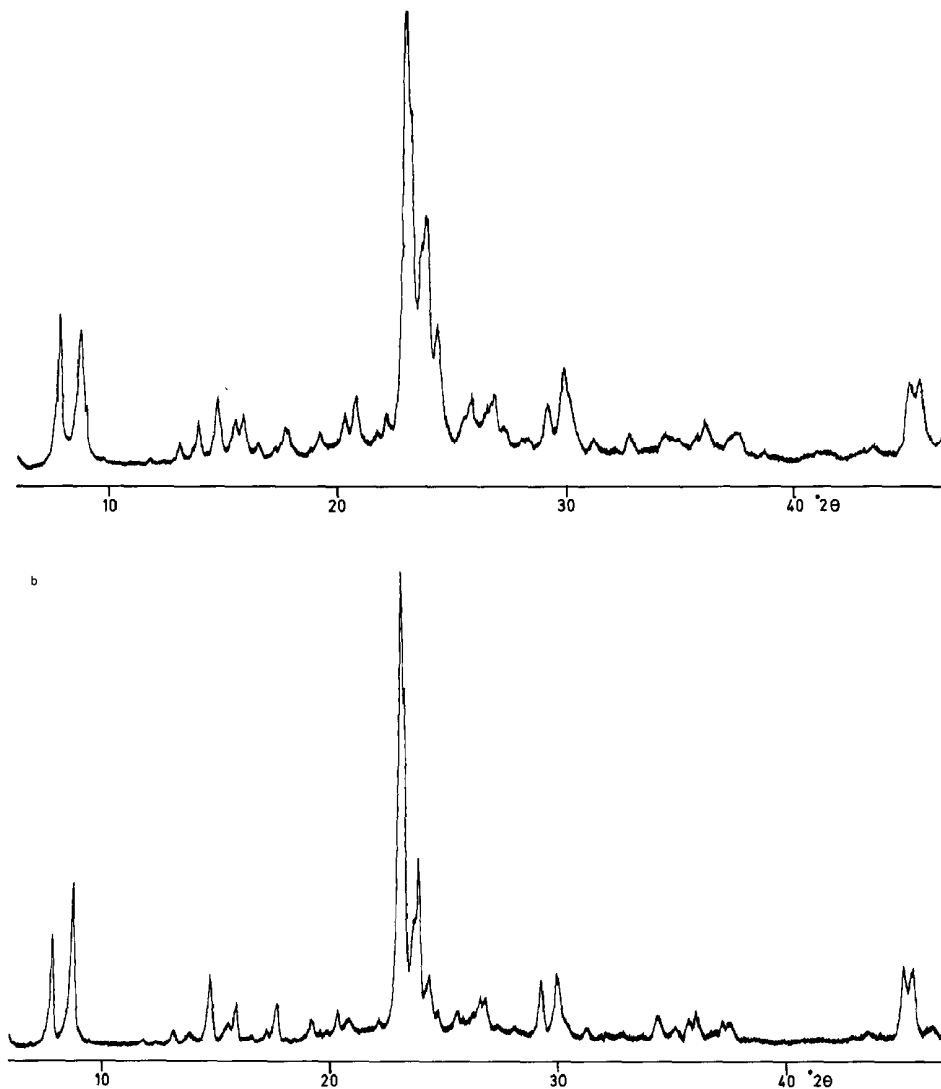


FIG. 1. Intensity of X-ray reflections as a function of angle 2Θ , obtained with powder diffraction APD-10 (Philips) using monochromatic $\text{CuK}\alpha$ radiation. (a) Pentasil I; (b) mixture of Pentasil II + III before classification.

samples at temperatures between 293 and 333 K. The specific equilibrium uptake at a given temperature and pressure and also the form of the equilibrium isotherm, however, were found to depend for certain sorbates markedly on the method of preparation of the zeolite and also to a minor extent on the crystal size. This observation is exemplified in Fig. 2 where equilibrium isotherms of methanol for two temperatures are shown for Pentasil I and III and in

Fig. 3 where the equilibrium isotherms of ethane are compared for zeolite samples from the same batch but with different crystal size (II and III). Characteristic data of isotherms are summarized in Table 2, namely,

(1) the slope $K = (1/m_z) \cdot (dn_s/dp)$ of the isotherm at a given temperature at the origin ($p \rightarrow 0$);

(2) the differential heat ΔH_s of sorption at low degrees of loading, calculated from the

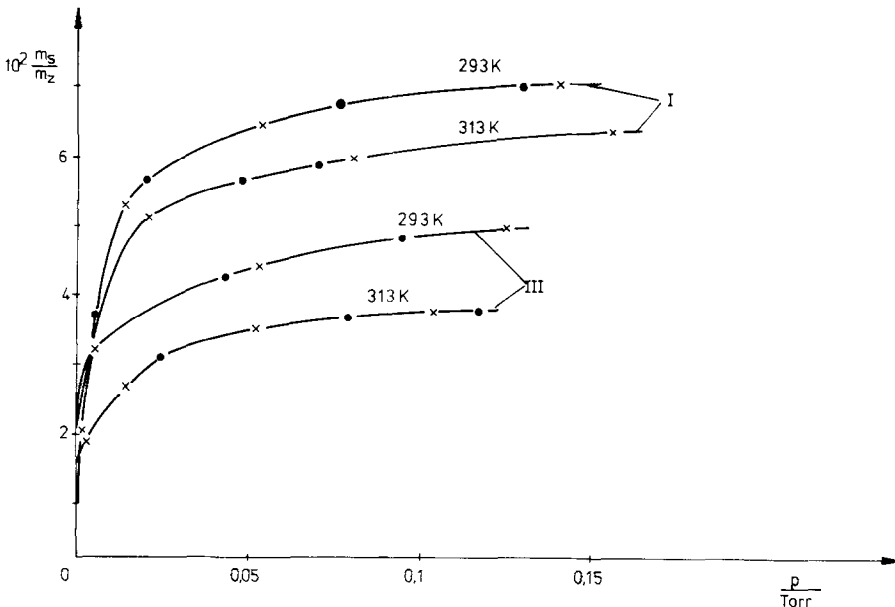


FIG. 2. Isotherms of sorption (●) and desorption (×) of methanol in Pentasil I and III.

temperature coefficient of the initial slope K of the isotherm

$$\Delta H_s = \frac{d \ln K}{dT} RT^2;$$

(3) the uptake at a pressure where the sorbed amount becomes nearly pressure

independent, giving an indication of the sorption capacity.

Both the slope of the isotherms and the sorption capacities at saturation in the smaller crystals (sample II) are greater by a factor of about 1.5 to 2 than the respective values for the same sorbate in larger crys-

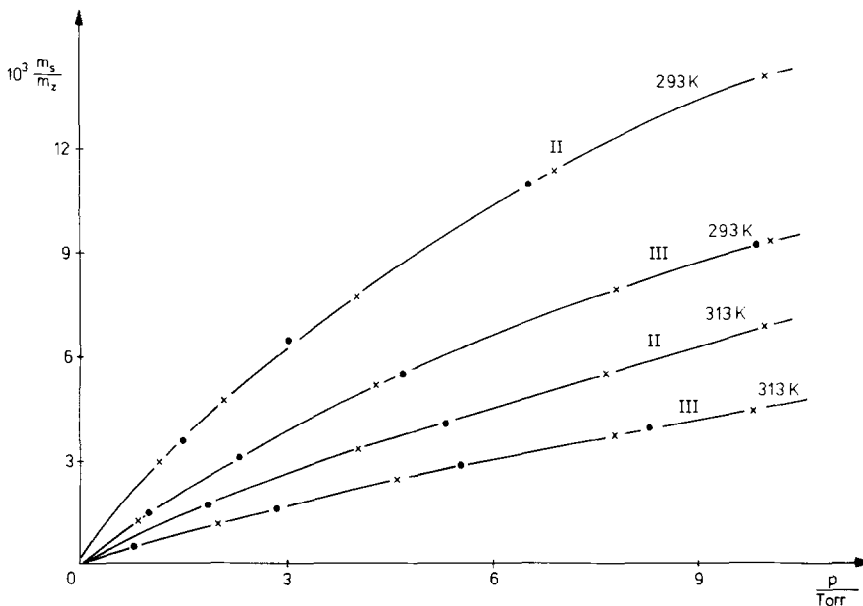


FIG. 3. Isotherms of sorption (●) and desorption (×) of ethane at 293 and 313 K in Pentasil II and III.

TABLE 2
Isotherm Data for Sorption in Pentasil I, II, and III

Sorbate	Property	I	II	III
C ₂ H ₆	K at 293 K (mol/g Pa)		5.75×10^{-7}	3×10^{-7}
	ΔH_S (kJ/mol)		-42.7	-37.5
	$\frac{n_s}{m_z}$ at 293 K (mol/g) $p = 4$ mbar		2.1×10^{-4}	1.28×10^{-4}
C ₃ H ₈	K at 293 K (mol/g Pa)		1.4×10^{-5}	6.38×10^{-6}
	ΔH_S (kJ/mol)		-44	-42.8
	$\frac{n_s}{m_z}$ at 293 K (mol/g) $p = 0.67$ mbar		3.88×10^{-4}	2.75×10^{-4}
<i>n</i> -C ₄ H ₁₀	K at 293 K (mol/g Pa)			6.8×10^{-6}
	ΔH_S (kJ/mol)			-47
	$\frac{n_s}{m_z}$ at 293 K (mol/g) $p = 1.6$ mbar			5.17×10^{-4}
<i>n</i> -C ₅ H ₁₂	K at 293 K (mol/g Pa)			6.26×10^{-4}
	ΔH_S (kJ/mol)			-54
	$\frac{n_s}{m_z}$ at 293 K (mol/g) $p = 2.7 \times 10^{-2}$ mbar			5.56×10^{-4}
<i>n</i> -C ₆ H ₁₄	K at 293 K (mol/g Pa)	5.44×10^{-4}	2.5×10^{-3}	1.52×10^{-3}
	$\frac{n_s}{m_z}$ at 293 K (mol/g) $p = 0.13$ mbar	2.73×10^{-4}	1.28×10^{-3}	8.41×10^{-4}
	K at 293 K (mol/g Pa)	10^{-4}	—	—
C ₂ H ₄	ΔH_S (kJ/mol)	-54	—	—
	$\frac{n_s}{m_z}$ at 293 K (mol/g) $p = 0.13$ mbar	6×10^{-4}	—	—
	K at 293 K (mol/g Pa)	2.93×10^{-3}		
Methanol	$\frac{n_s}{m_z}$ at 293 K (mol/g) $p = 6.7 \times 10^{-2}$ mbar	2×10^{-3}		
	K at 293 K (mol/g Pa)	2.04×10^{-3}		9.5×10^{-4}
	ΔH_S (kJ/mol)			-20.3
Dimethyl ether	$\frac{n_s}{m_z}$ at 293 K (mol/g) $p = 0.13$ mbar	1.41×10^{-3}		8.59×10^{-4}
	K at 293 K (mol/g Pa)		4.5×10^{-4}	3.2×10^{-4}
	$\frac{n_s}{m_z}$ at 293 K (mol/g) $p = 0.13$ mbar		7.44×10^{-4}	5.9×10^{-4}

tals of the same preparation (sample III). It therefore appears that the nature of the interaction between sorbate and zeolite is independent of crystal size but that the

internal volume accessible to the sorbate per unit of mass of zeolite is greater in the smaller crystals.

For dimethyl ether, benzene, and *m*-

xylene, diffusivities of the sorbate in the crystals could be obtained from the rates of sorption and desorption as described previously (15, 16). The influence of intercrystalline mass transfer and of heat transfer on the initial rate was eliminated through variation of sample geometry. The kinetics of sorption of benzene in a monolayer of crystals of sample III are shown in Fig. 4 as an example. The following intracrystalline diffusivities were obtained with larger mono-disperse crystals (sample III).

Sorbate	$D/(\text{cm}^2/\text{sec})$	
	293 K	313 K
Dimethyl ether	1.2×10^{-9}	1.5×10^{-9}
Benzene	2.3×10^{-10}	2.5×10^{-10}
<i>M</i> -Xylene	2.2×10^{-10}	2.4×10^{-10}

The kinetics of sorption of methanol and lower paraffins are characterized by a very rapid initial uptake which could not be resolved due to the limited response time of the equipment, followed by a slower sorption process which is initially linear in $t^{1/2}$.

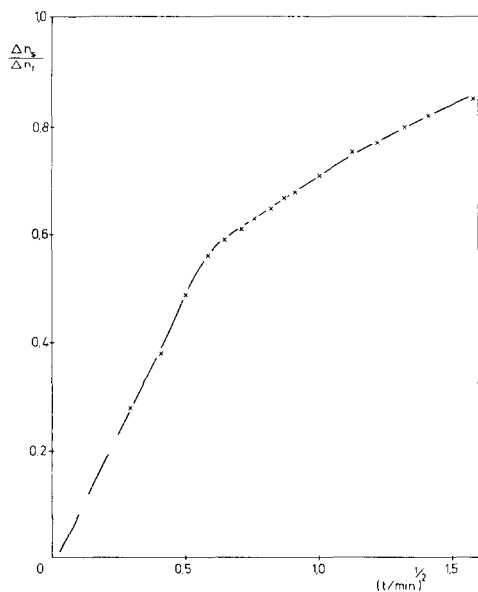


FIG. 4. Kinetics of sorption at 293 K of benzene in Pentasil III starting at $n_0 = 0$ mmol and $p_0 = 0.42$ mbar; the equilibrium values are $n_t = 9.1 \times 10^{-3}$ mmol and $p_t = 0.24$ mbar, $m_z = 16.5$ mg.

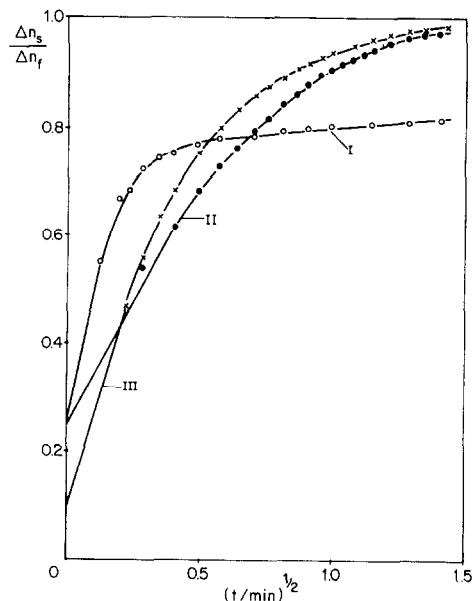


FIG. 5. Kinetics of sorption of *n*-hexane in Pentasil I (○), II (●), and III (×) at 293 K starting at $n_0 = 0$, initial and final pressures (p_0 , p_t), final loading n_t at equilibrium. I: $p_0 = 0.39$ mbar; $n_t = 6.15 \times 10^{-3}$ mmol; $p_t = 0.27$ mbar, $m_z = 21.85$ mg; II: $p_0 = 0.42$ mbar; $n_t = 2.66 \times 10^{-2}$ mmol; $p_t = 0.1$ mbar, $m_z = 21.18$ mg; III: $p_0 = 0.4$ mbar; $n_t = 1.37 \times 10^{-2}$ mmol; $p_t = 0.26$ mbar, $m_z = 16.14$ mg.

This behaviour is illustrated in Fig. 5 for *n*-hexane as an example. The rapid initial uptake cannot be due to external adsorption on the surface of the crystals since its amount corresponds to at least 85 monolayers on the external surface at $p/p_{\text{sat}} < 1.9 \times 10^{-3}$. Such kinetic behaviour would be expected for a heterogeneous sorbent, consisting of crystallites characterized by different diffusivities of the sorbate. However, on the basis of the present observations one cannot decide unequivocally whether the kinetically distinct processes occur in parallel or in series. In the case of ethene, sorption was reversible in Pentasil I, whereas it turned out to be irreversible at 353 K in Pentasil III.

(b) Irreversible Sorption of Olefins and Cyclohexane

The sorption of ethene, propene, and cyclohexane in Pentasil II and III was

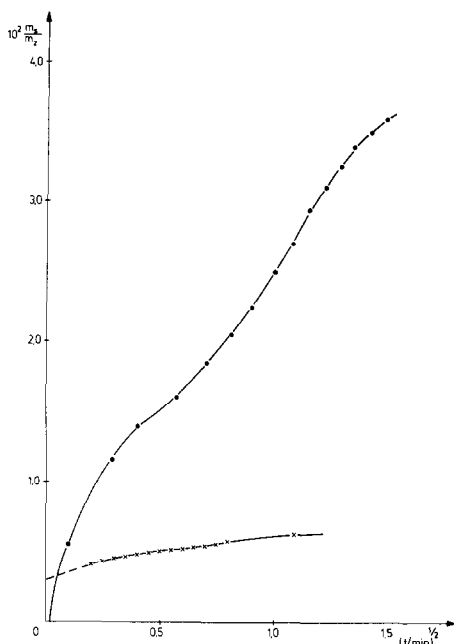


FIG. 6. Kinetics of sorption of propane (×) and propene (●) in Pentasil III at 293 K starting at $n_0 = 0$ mmol and $p_0 = 0.86$ mbar; the equilibrium values for propane in Pentasil III are $n_t = 1.8 \times 10^{-2}$ mmol and $p_t = 0.5$ mbar, $m_z = 91.75$ mg.

found to be irreversible; these systems cannot be described by equilibrium isotherms. Only by evacuating at 613 K was the sorbate removed and the sorption capacity of the zeolite restored in these cases. The amounts of uptake were much greater in these systems compared to the reversible sorption of compounds of similar molecular weight (e.g., propene vs propane or cyclohexane vs benzene) and the kinetics are markedly different in the reversible as compared to the irreversible systems, as shown in Figs. 6 and 7. The initial uptake in these irreversible systems is not linear in $t^{1/2}$; an induction period is frequently observed and equilibrium is not reached after several hours. The kinetics in these systems cannot be described or approximately represented as a simple diffusion process.

Rather pronounced differences are observed in the sorption behaviour of Pentasil zeolites of different origins with respect to these sorbates. As an example the kinetics

of sorption of propene in Pentasil I and in Pentasil III are shown in Fig. 8.

(c) Catalytic Conversion of Methanol

The kinetics of conversion of methanol were studied between 388 and 473 K on Pentasil I and at 585 K on Pentasil II.

In the temperature range below 473 K only dimethyl ether was observed as a product. The kinetics of the reaction can be described for Pentasil I by the rate equation

$$r = \frac{-\dot{n}_{\text{CH}_3\text{OH}}}{m_z} = \frac{k_1 \cdot p_{\text{CH}_3\text{OH}}}{1 + k_2 \cdot p_{\text{H}_2\text{O}}}$$

with

$$k_1 = 6 \times 10^5 \exp \frac{-80 \text{ kJmol}^{-1}}{RT} \frac{\text{mol}}{\text{g} \cdot \text{sec} \cdot \text{bar}}$$

At 585 K and $p_{\text{CH}_3\text{OH}} = 0.03$ bar the following rates of formation of different compounds were observed in the differential reactor with Pentasil II (all rates are specified per gram of catalyst and the meth-

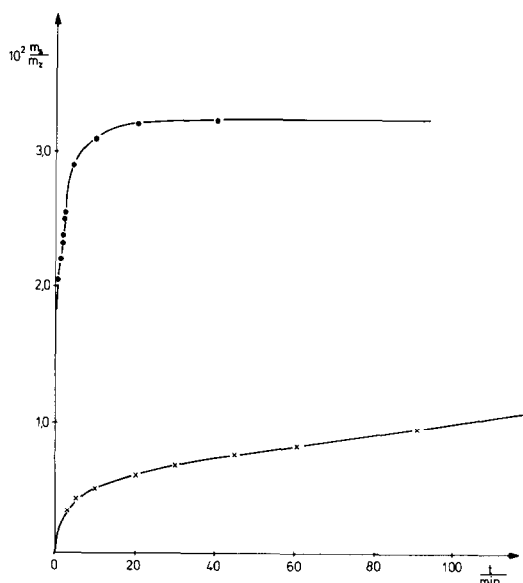


FIG. 7. Kinetics of sorption of benzene (●) and cyclohexane (×) in Pentasil III at 293 K starting at $n_0 = 0$ mmol, $p_0 = 0.5$ mbar; the equilibrium values for benzene in Pentasil III are $n_t = 1.31 \times 10^{-2}$ mmol and $p_t = 0.27$ mbar, $m_z = 84.75$ mg.

anol conversion rate was 2.4×10^{-5} mol g⁻¹ sec⁻¹):

Dimethyl ether	7.5×10^{-6}	mol g ⁻¹ sec ⁻¹
Ethene	1.4×10^{-6}	mol g ⁻¹ sec ⁻¹
Propene	1.2×10^{-6}	mol g ⁻¹ sec ⁻¹
C ₄	3.3×10^{-7}	mol g ⁻¹ sec ⁻¹
C ₅₊	7.5×10^{-8}	mol g ⁻¹ sec ⁻¹
Alkylaromatics	1.1×10^{-7}	mol g ⁻¹ sec ⁻¹

The predominating primary product of methanol conversion is thus gaseous dimethyl ether, as has already been shown by Chang and Silvestri (3) and by other authors (4, 9). Since this reaction is fast compared to the subsequent conversion of dimethyl ether to hydrocarbons only the latter and the reactions of olefins to higher

hydrocarbons (which may be important in a network of consecutive reactions) were studied in more detail in the differential reactor.

(d) *Catalytic Conversion of Dimethyl Ether and of Lower Olefins*

Rates of formation of different hydrocarbons from dimethyl ether, from ethene, and from propene were observed at two temperatures (558 and 585 K), the catalyst being in contact with a feedstream of nearly constant partial pressure of reactant (differential reactor). Results for three Pentasil catalysts of different origin or crystallite size but the same pellet geometry (4 mm diameter, 2.5-mm thickness) are listed in Table 3. From these data the product distri-

TABLE 3

Rates \dot{n}_i/m_2 of Formation of Different Products i in the Differential Reactor, Values in mol g⁻¹ sec⁻¹

Product i	$T = 558$ K			$T = 585$ K		
	Cat. I	Cat. II	Cat. III	Cat. I	Cat. II	Cat. III
Reactant: CH ₃ OCH ₃ , $\bar{p}_{\text{CH}_3\text{OCH}_3} = 0.03$ bar, pellet size: $\bar{r} = 0.2$ cm						
C ₂ H ₄	7.8×10^{-7}	6.1×10^{-7}	6.1×10^{-7}	1.1×10^{-6}	8.3×10^{-7}	8.3×10^{-7}
C ₃ H ₆	5.0×10^{-7}	5.6×10^{-7}	5.6×10^{-7}	1.1×10^{-6}	1.3×10^{-6}	1.2×10^{-6}
C ₄ H ₈	2.8×10^{-6}	3.9×10^{-6}	4.2×10^{-6}	5.8×10^{-6}	1.0×10^{-7}	1.1×10^{-7}
C ₄ -par.	8.2×10^{-8}	9.1×10^{-8}	7.8×10^{-8}	1.8×10^{-7}	2.6×10^{-7}	2.0×10^{-7}
C ₅	3.1×10^{-8}	3.1×10^{-8}	2.6×10^{-8}	8.3×10^{-8}	9.7×10^{-8}	8.1×10^{-8}
C ₆ + aliph.	4.5×10^{-8}	5.3×10^{-8}	5.0×10^{-8}	1.1×10^{-7}	1.6×10^{-7}	1.3×10^{-7}
<i>m</i> -Xylene	1.7×10^{-8}	1.3×10^{-8}	1.3×10^{-8}	9.7×10^{-8}	8.6×10^{-8}	6.4×10^{-8}
C ₈ + alk. arom.	3.3×10^{-8}	2.8×10^{-8}	2.7×10^{-8}	5.8×10^{-8}	5.0×10^{-8}	4.2×10^{-8}
Rate of conversion of reactant CH ₃ OCH ₃	2.2×10^{-6}	2.1×10^{-6}	2.1×10^{-6}	4.5×10^{-6}	4.8×10^{-6}	4.4×10^{-6}
Reactant: C ₂ H ₄ , $\bar{p}_{\text{C}_2\text{H}_4} = 0.03$ bar, pellet size: $\bar{r} = 0.2$ cm						
C ₃ H ₆	1.3×10^{-7}	1.8×10^{-7}	1.1×10^{-7}	2.4×10^{-7}	2.2×10^{-7}	1.1×10^{-7}
C ₄ H ₈	3.6×10^{-8}	5.5×10^{-8}	2.6×10^{-8}	5.5×10^{-8}	6.1×10^{-8}	2.8×10^{-8}
C ₄ -par.	1.7×10^{-8}	2.3×10^{-8}	1.3×10^{-8}	4.2×10^{-8}	2.8×10^{-8}	1.6×10^{-8}
C ₅	8.9×10^{-9}	1.3×10^{-8}	6.1×10^{-9}	1.6×10^{-8}	1.4×10^{-8}	8.3×10^{-9}
C ₆ + aliph.	1.3×10^{-8}	1.6×10^{-8}	5.8×10^{-9}	2.1×10^{-8}	1.8×10^{-8}	6.7×10^{-9}
<i>m</i> -Xylene	$<2.8 \times 10^{-9}$	$<2.8 \times 10^{-9}$	$<2.8 \times 10^{-9}$	$<2.8 \times 10^{-9}$	$<2.8 \times 10^{-9}$	$<2.8 \times 10^{-9}$
C ₈ + alk. arom.	5.0×10^{-9}	2.8×10^{-9}	$<2.8 \times 10^{-9}$	8.9×10^{-9}	3.9×10^{-9}	2.8×10^{-9}
Rate of conversion of reactant C ₂ H ₄	4.1×10^{-7}	5.5×10^{-7}	3.0×10^{-7}	7.0×10^{-7}	6.3×10^{-7}	3.2×10^{-7}
Reactant: C ₃ H ₆ , $\bar{p}_{\text{C}_3\text{H}_6} = 0.03$ bar, pellet size: $\bar{r} = 0.2$ cm						
C ₂ H ₄	8.9×10^{-8}	1.3×10^{-7}	1.1×10^{-7}	2.2×10^{-7}	3.3×10^{-7}	3.1×10^{-7}
C ₄ H ₈	1.3×10^{-6}	1.8×10^{-6}	1.7×10^{-6}	1.6×10^{-6}	2.3×10^{-6}	2.2×10^{-6}
C ₄ -par.	1.0×10^{-6}	1.5×10^{-6}	1.4×10^{-6}	1.2×10^{-6}	1.6×10^{-6}	1.6×10^{-6}
C ₅	7.5×10^{-7}	9.7×10^{-7}	9.4×10^{-7}	7.8×10^{-7}	1.1×10^{-6}	8.9×10^{-7}
C ₆ + aliph.	1.1×10^{-6}	1.6×10^{-6}	1.5×10^{-6}	1.0×10^{-6}	1.5×10^{-6}	1.3×10^{-6}
<i>m</i> -Xylene	$<8.3 \times 10^{-9}$	$<8.3 \times 10^{-9}$	$<8.3 \times 10^{-9}$	2.2×10^{-8}	3.3×10^{-8}	2.8×10^{-8}
C ₈ + alk. arom.	$<8.3 \times 10^{-9}$	$<8.3 \times 10^{-9}$	$<8.3 \times 10^{-9}$	4.2×10^{-8}	6.2×10^{-8}	5.3×10^{-8}
Rate of conversion of reactant C ₃ H ₆	7.0×10^{-8}	1.0×10^{-7}	9.0×10^{-8}	7.3×10^{-8}	1.1×10^{-7}	1.0×10^{-7}

TABLE 4

Product Distributions in the Differential Reactor; Percentage of Carbon in Different Products or Product Groups

Product	T = 558 K			T = 585 K		
	Cat. I	Cat. II	Cat. III	Cat. I	Cat. II	Cat. III
Reactant: CH ₃ OCH ₃ , $\bar{p}_{\text{CH}_3\text{OCH}_3} = 0.03$ bar, pellet size: $\bar{r} = 0.2$ cm						
C ₂ H ₄	35.4	28.4	29.0	24.6	17.0	19.1
C ₃ H ₆	34.1	39.1	39.9	36.9	40.0	41.4
C ₄ H ₈	2.5	3.6	4.0	2.6	4.1	5.1
C ₄ -par.	7.5	8.4	7.4	8.1	10.7	9.2
C ₅	3.5	3.6	3.1	4.6	5.0	4.6
C ₆ ⁺ aliph.	7.2	8.6	8.3	8.6	11.5	10.4
<i>m</i> -Xylene	3.1	2.4	2.5	8.7	7.1	5.9
C ₈ ⁺ alk. arom.	6.7	5.9	5.8	5.9	4.6	4.3
Reactant: C ₃ H ₆ , $\bar{p}_{\text{C}_3\text{H}_6} = 0.03$ bar, pellet size: $\bar{r} = 0.2$ cm						
C ₂ H ₄	0.8	0.9	0.8	1.9	2.0	2.0
C ₄ H ₈	24.8	24.3	24.3	27.7	27.8	29.3
C ₄ -par.	19.1	20.2	20.0	20.8	19.3	21.3
C ₅	17.9	16.3	16.8	16.9	16.6	14.8
C ₆ ⁺ aliph.	36.7	37.8	37.6	30.3	31.8	30.3
<i>m</i> -Xylene	0.3	0.2	0.2	0.8	0.8	0.7
C ₈ ⁺ alk. arom.	0.4	0.3	0.3	1.6	1.7	1.6

bution under the reaction conditions specified can be computed. In Table 4 product distributions as percentages of carbon in different products are shown for dimethyl ether and for propene as reactants.

Pellets consisting of Pentasil II and pellets of Pentasil III were crushed and sieved to particles of approx 1 mm diameter in order to study the influence of intercrystalline diffusion (pellet size) on the rate of reaction and on product distribution. With these catalyst pellets and with dimethyl ether as a reactant the rates of formation of different products listed in Table 5 were obtained; the corresponding product distributions (percentage of carbon in different product species) are given in Table 6.

DISCUSSION

Rather pronounced differences were observed between Pentasil zeolites of different origin or varying crystal size with respect to sorption behaviour, even though the X-ray powder diffraction patterns of samples I, II, and III appear to be almost

identical. It follows that these zeolites are not fully characterized by their composition and powder diffraction patterns, which is not surprising since from a thermodynamic viewpoint they must be regarded as metastable structures. Details of the structure of a solid which is not in thermodynamic equilibrium can depend on its previous history, whereas an equilibrium system is completely determined by composition, temperature, and pressure. There are many variables like periodicity of location of aluminum in the lattice or its partial removal near phase boundaries which may be responsible for differences in sorption behaviour and catalytic properties, besides the possibility of intergrowth of related structures described by Kokotailo and Meier (11). Pentasil I on the one hand and Pentasil II or III on the other hand appear to be quite unrelated materials as far as the sorption of propene at 293 K is concerned (Fig. 8); differences between these materials are much less pronounced, however, if one considers the catalytic properties in the conversion of dimethyl ether or lower

TABLE 5

Rates \dot{n}_i/m_z of Formation of Different Products i in the Differential Reactor, Values in $\text{mol g}^{-1} \text{sec}^{-1}$

Product i	585 K	575 K	567 K	558 K	548 K	538 K
Reactant: CH_3OCH_3 , $\bar{p}_{\text{CH}_3\text{OCH}_3} = 0.016$ bar, Cat. II, pellet size: $\bar{r} = 0.08$ cm						
C_2H_4	2.3×10^{-6}	1.7×10^{-6}	1.31×10^{-6}	7.7×10^{-7}	4.6×10^{-7}	4.2×10^{-7}
C_3H_6	4.1×10^{-6}	3.1×10^{-6}	2.26×10^{-6}	1.5×10^{-6}	9.0×10^{-7}	5.3×10^{-7}
C_4	9.1×10^{-7}	5.8×10^{-7}	4.0×10^{-7}	3.6×10^{-7}	2.2×10^{-7}	1.4×10^{-7}
C_5	2.0×10^{-7}	1.5×10^{-7}	9.3×10^{-8}	6.2×10^{-8}	2.3×10^{-8}	1.6×10^{-8}
C_6^+ aliph.	4.6×10^{-7}	3.5×10^{-7}	2.3×10^{-7}	1.7×10^{-7}	9.9×10^{-8}	6.6×10^{-8}
m -Xylene	7.7×10^{-8}	5.8×10^{-8}	4.3×10^{-8}	3.9×10^{-8}	1.9×10^{-8}	1.4×10^{-8}
C_8^+ alk. arom.	2.6×10^{-8}	1.8×10^{-8}	1.7×10^{-8}	8.6×10^{-9}	$< 4.3 \times 10^{-9}$	$< 3 \times 10^{-9}$
Rate of conversion of reactant CH_3OCH_3	1.28×10^{-5}	9.4×10^{-6}	6.8×10^{-6}	4.7×10^{-6}	2.8×10^{-6}	1.9×10^{-6}
	511 K	533 K	554 K	575 K	594.5 K	613.5 K
Reactant: CH_3OCH_3 , $\bar{p}_{\text{CH}_3\text{OCH}_3} = 0.03$ bar, Cat. III, pellet size: $\bar{r} = 0.05$ cm						
C_2H_4	2.1×10^{-7}	7.2×10^{-7}	1.4×10^{-6}	2.4×10^{-6}	3.7×10^{-6}	6.2×10^{-6}
C_3H_6	2.1×10^{-7}	7.5×10^{-7}	1.7×10^{-6}	3.8×10^{-6}	7.8×10^{-6}	1.6×10^{-5}
C_4			2.0×10^{-7}	5.2×10^{-7}	1.4×10^{-6}	2.7×10^{-6}
C_5			4.0×10^{-8}	1.2×10^{-7}	4.1×10^{-7}	8.2×10^{-7}
C_6^+ aliph.			9.0×10^{-8}	2.8×10^{-7}	6.4×10^{-7}	1.0×10^{-6}
Arom.			3.0×10^{-8}	8.6×10^{-8}	1.5×10^{-7}	3.0×10^{-7}
Rate of conversion of reactant CH_3OCH_3	2.2×10^{-6}	3.7×10^{-6}	6.6×10^{-6}	1.5×10^{-5}	2.3×10^{-5}	4.5×10^{-5}
	594.5 K	613.5 K	633 K			

olefins at elevated temperatures (Tables 3 and 4). Production of ethene from dimethyl ether is predominating on Pentasil I, whereas propene is the preferred product

on Pentasil II and III, but the differences between the rates of formation of any product species on different catalysts never exceed a factor of 2 under given operating

TABLE 6

Product Distributions in the Differential Reactor; Percentage of Carbon in Different Products or Product Groups

Product i	585 K	575 K	567 K	558 K	548 K	538 K
Reactant: CH_3OCH_3 , $\bar{p}_{\text{CH}_3\text{OCH}_3} = 0.016$ bar, Cat. II, pellet size: $\bar{r} = 0.08$ cm						
C_2H_4	18.0	18.1	19.2	16.4	16.7	23.4
C_3H_6	48.1	49.5	49.8	48.0	49.1	44.0
C_4	14.2	12.2	11.9	15.4	16.0	14.8
C_5	3.9	4.0	3.4	3.3	2.1	2.1
C_6^+ aliph.	12.5	12.8	11.9	12.8	12.6	12.6
m -Xylene	2.4	2.5	2.7	3.3	2.8	3.0
C_8^+ alk. arom.	0.9	0.9	1.1	0.8	0.7	0.1
	594.5 K	613.5 K	633 K			
Reactant: CH_3OCH_3 , $\bar{p}_{\text{CH}_3\text{OCH}_3} = 0.03$ bar, Cat. III, pellet size: $\bar{r} = 0.05$ cm						
C_2H_4	16	14	13			
C_3H_6	51	53	52			
C_4	13	12	14			
C_5	4	5	6			
C_6^+ aliph.	10	8	11			
Arom.	3	3	3			

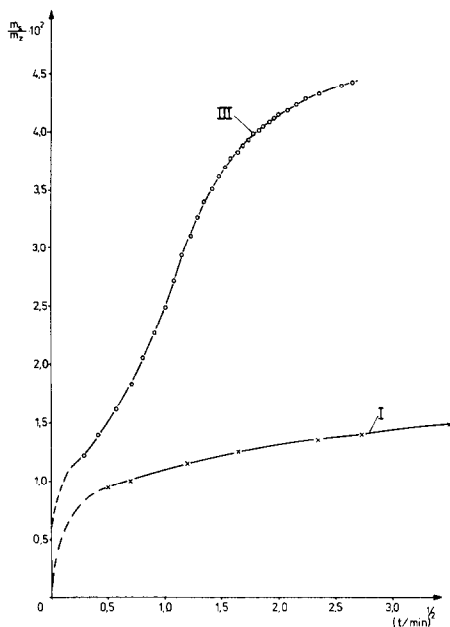


FIG. 8. Kinetics of sorption of propene in Pentasil I and Pentasil III at 293 K starting at $n_0 = 0$ mmol and $p_0 = 0.95$ mbar; the equilibrium values for propene in Pentasil I are $n_t = 1.62 \times 10^{-2}$ mmol and $p_t = 0.81$ mbar, $m_z = 39.95$ mg.

conditions. However, it must be noted that differences in the intrinsic kinetics will be attenuated if the efficiency of the pellet in the conversion of primary reactants is much smaller than unity due to a limited rate of *intercrystalline* mass transfer. With catalyst pellets of 2.5×4 mm diameter the highest rate of conversion of reactant observed was of the order of 1.1×10^{-5} mol/sec (cm^3 of catalyst pellet) (propene on Pentasil II at 585 K) and with an effective diffusivity in the intercrystalline voids of the pellets of $10^{-2} \text{ cm}^2 \text{ sec}^{-1}$ a Weisz number of 5 follows (20). Under these conditions the observed activities, as well as the selectivities, will depend on pellet geometry and secondary pore structure. The selectivities listed in Tables 3 and 4, therefore, have to be considered as instantaneous or point selectivities, characteristic of the *pellets* under consideration. If these pellets are crushed to a size with linear dimensions under 0.8 mm different

rates of reaction and different product distributions are observed, as illustrated in Figs. 9 and 10 for Pentasil II. At 538 K the rate of conversion of dimethyl ether observed with the smaller pellets was $1.9 \times 10^{-6} \text{ mol g}^{-1} \text{ sec}^{-1}$; for this rate of reaction a Weisz number of 0.5 is calculated. The influence of intercrystalline mass transfer on the kinetics of conversion of $(\text{CH}_3)_2\text{O}$ was thus nearly eliminated with the smaller pellets. The influence of intercrystalline mass transfer on the reaction network and product distribution will be the object of a detailed future publication.

The question of the influence of *intra*-crystalline mass transfer in the zeolites on selectivity and activity appears to be rather difficult to answer in a general way. However, on the basis of the present data it can be shown that intracrystalline diffusion should have no influence on the rate of conversion of dimethyl ether at temperatures below 600 K.

For dimethyl ether (E) in Pentasil III ($R = 7 \mu\text{m}$) we have from the sorption kinetics $R^2/D_E \leq 200 \text{ sec}$ at 575 K, whereas from

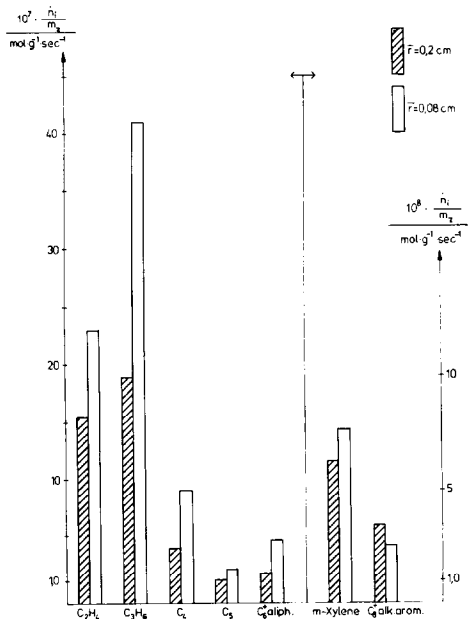


FIG. 9. Rates of formation of different products; pellets of different size; reactant: CH_3OCH_3 , $\bar{p}_{\text{CH}_3\text{OCH}_3} = 0.016$ bar, Pentasil II, $T = 585$ K.

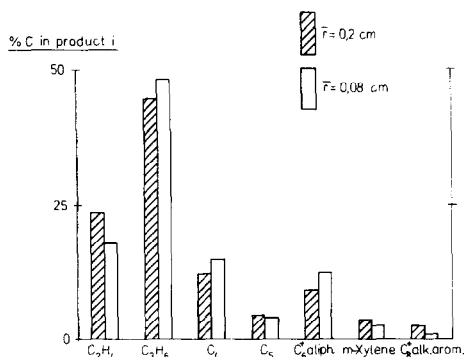


FIG. 10. Product distributions in the differential reactor (% of carbon in different products or product groups); pellets of different size; reactant: CH_3OCH_3 , $\bar{P}_{\text{CH}_3\text{OCH}_3} = 0.016$ bar Pentasil II, $T = 585$ K.

equilibrium isotherms and their temperature dependence (Table 2) an intracrystalline concentration of dimethyl ether of $n_E/V_Z \approx 10^{-3}$ mol/cm³ follows at $P_{\text{CH}_3\text{OCH}_3} = 0.03$ bar and $T = 575$ K. A rate of conversion of CH_3OCH_3 of 1.5×10^{-5} mol g⁻¹ sec⁻¹ $\hat{=} 3 \times 10^{-5}$ mol cm⁻³ sec⁻¹ was observed at 575 K and $P_{\text{CH}_3\text{OCH}_3} = 0.03$ bar. With these data we have for the intracrystalline Weisz number W_Z

$$W_Z = \frac{R^2}{9D_E} \cdot \frac{V_Z}{n_E} \cdot \left(\frac{1}{V_Z} \cdot \frac{-dn_E}{dt} \right) \\ \leq \frac{200}{9} \cdot \frac{3 \times 10^{-5}}{10^{-3}} = 0.7.$$

The rate of conversion should be practically unaffected ($\eta > 0.9$) by intracrystalline diffusion if W_Z is smaller than 1.

This result is consistent with the observation that the rate of conversion of dimethyl ether is independent of crystal size, identical within experimental error for catalysts II and III. It should be noted, however, that catalysts II and III are not only different with respect to crystal size but also with respect to their composition ($\text{SiO}_2 : \text{Al}_2\text{O}_3$), although they are obtained from the same batch. The rate of conversion of CH_3OCH_3 seems to be generally almost independent of the $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratio in the catalyst within the range investigated (Table 3).

Since the product distribution in the reaction of dimethyl ether and of propene appears to be the same for catalysts II and III and thus to be independent of crystal size, one is inclined to conclude that no concentration gradients exist also for subsequently formed materials in these crystals. However, the rate of formation of the main products from ethene is markedly different for these two catalysts. Furthermore it remains unclear at the moment to what extent the classical concept of superposition of random diffusion and reaction can be applied to reactions of olefins in these zeolites where the kinetics of sorption of C_2H_4 and C_3H_6 cannot be understood as a simple process of diffusion.

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