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“Coking” of zeolites during methanol conversion: Basic reactions of the MTO-, MTP- and MTG processes

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ABSTRACT

Deactivation of acidic zeolite catalysts during methanol conversion is investigated for elucidating how spatial constraints interfere mechanistically. Detailed product composition – including retained organic matter – is determined in a time resolved mode.

At 270–300 °C with H-ZSM-5, first unsaturated hydrocarbons are formed—methane being the indicative co-product. Then the reaction rate increases auto-catalytically, but soon declines because of exhaustive pore filling. The retained organic matter consists mainly of ethyl-trimethyl-benzene- and isopropyl-dimethyl-benzene molecules. Alkylation of benzene rings with ethene and propene produces the deactivating molecules.

At 475 °C, alkylation of benzene rings with olefins has shifted to the reverse, reactivating the H-ZSM-5 catalyst. Coke forms slowly on the surface of H-ZSM-5 crystallites. Spatial constraints suppress the formation of 2-ring aromatics. With the wide pore zeolite H-Y, fast deactivation is noticed—bigger aromatic molecules can be formed and are retained.

Methanol reactions on the protonic catalyst sites are visualized as CH_3+ attack for methylation and dehydrogenation, methane being the hydrogen-rich co-product. Methanol conversion on zeolites H-ZSM-58, H-EU-1 and H-Beta is comparatively investigated.

Zone ageing is discussed for favorable reactor design.

It is shown, how a multi-compound product composition is the source of information for elucidating complex reaction mechanisms.

1. Introduction

The conversion of methanol to hydrocarbons on acidic zeolites is mechanistically complex—a topic of ongoing debate [1–17]. Understanding deactivation of the catalyst, needs knowledge about the reaction mechanism. Terms as “supra molecular origins of selectivity”, “reaction centers” [3] and “hydrocarbon pool” [4] have been proposed. It would be of interest to elucidate the principle parameters ruling the complexity. In recent In Situ IR-studies the retained organic matter on zeolite H-ZSM-5 during methanol conversion has been characterized [5]. Also In Situ NMR-studies have been performed [6] and micro-balance coke-formation-rate measurements have been reported [7].

Immense knowledge about catalyst deactivation by coking has been acquainted by Guisnet et al. [8–10] adding up influences as catalyst properties (dimensions of channels and cavities of zeolites, activity/acidity of sites, Si/Al-ratio, crystallite size and reaction conditions) (temperature and concentrations, reaction time and kind of reactants as paraffins, olefins, aromatics and methanol). It can be imagined that every kinetic regime must be explored individually. MTO (methanol to olefins) on H-SAPO-34 has been also investigated [11–13]. Due to narrower channel diameter than with H-ZSM-5, reaction mechanism and deactivation mechanism appear to be different (side chain methylation, exhaustive benzene-ring methylation, merely aromatics in the volatile reaction product but retained on the catalyst).

This article concentrates on methanol conversion on acidic zeolites addressing detailed product composition – including the organic matter on/in the catalyst – as depending on time. The particular interest is on methanol conversion on zeolite H-ZSM-5, but is studied with further zeolites also.

History of the problem begins in 1972 with synthesis of zeolite ZSM-5 (Argauer and Landolt), followed by resolution of its structure (Kokotailo), observation of gasoline formation from methanol (Chang: methanol to gasoline process [18]), understanding of shape selectivity to control diffusion (Weiß) and the postulate of transition state selectivity (Csicsery). Initially, a carbene type CH_2-addition for chain growth was proposed. Later the proton acidity of the catalyst and respective carbenium ion chemistry was recognized. Focusing on the activation of methanol, van Hoof imagined

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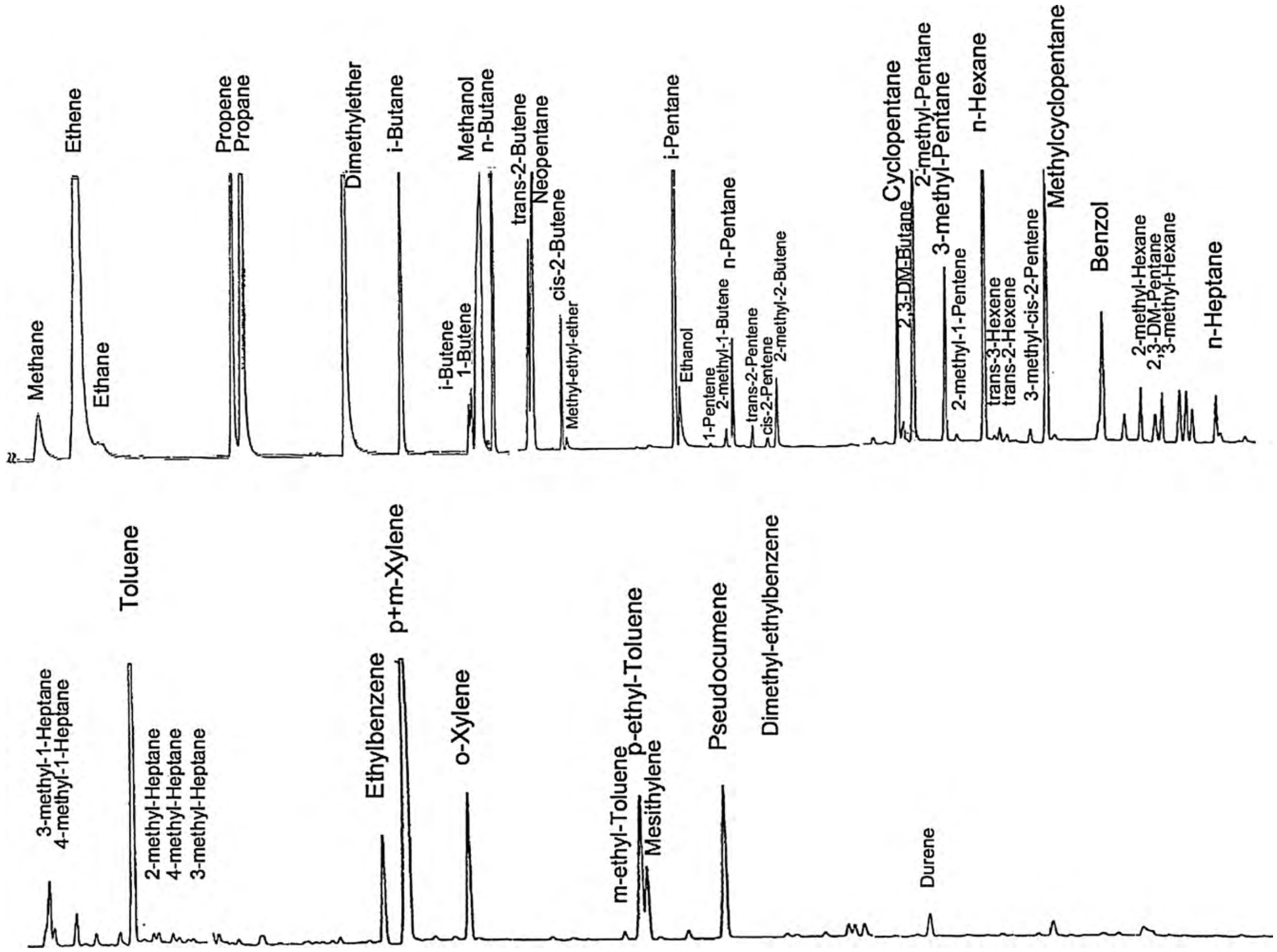


Fig. 1. Gas chromatogram of a product from methanol conversion on zeolite H-ZSM-5. Ampoule sample, taken from the product flow at ca. 200 °C, methanol conversion at 270 °C, sample taken at time-on-stream 92 min, gas chromatography conditions: capillary 100 m/0.25 mm, methyl silicon cross-linked, temperature programmed −80 to 262 °C.

a trimethyl oxonium rearrangement for "first carbon/carbon bond formation" [19]. But this seams to be relevant only during incubation at low temperature. Today, the synthesis of olefins from methanol is of industrial interest, the (secondary) formation of aromatics should be suppressed (MTO process, methanol to olefins, UOP-North-Hydro [20]; MTP-process, methanol to propylene, Lurgi [21]). Knowledge about the mechanism of catalyst deactivation is relevant for catalyst- and process-development.

In this article elemental reactions of deactivation – due to the organic matter being retained on the catalyst – are studied as depending on time-on-stream, using our, respectively, developed methods. Selectivity depends on many parameters, but the pattern of deactivation should remain the same for a distinct zeolite structure. The principle prerequisite for proposing a reaction mechanism – knowing the product composition in detail – is not easily attained for the methanol to olefin conversion. Problems are (1) too many compounds in the reaction product, (2) retained matter on/in the catalyst must be regarded as a product, yield and composition should be known and (3) product composition changes with time, but should be measured, as organic matter accumulates on/in the catalyst.

2. Experimental

Methods have been developed for time resolved measurement of selecivities and yields during methanol conversion. Capillary gas chromatography was adapted to detect all volatile compounds from methane up to e.g. C_{15} in the same chromatogram, beginning with a temperature program at −80 °C and ending at 270 °C (Fig. 1) [22–24], needing about 1 h. For attaining time resolution, quick product sampling in little pre-evacuated ampoules, which could be stored for later analysis was developed (Fig. 2) [22–23].

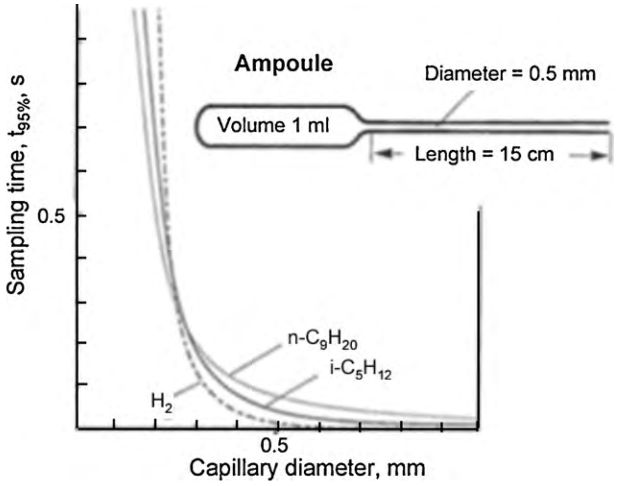


Fig. 2. Ampoule sampling; calculated 95% filling time of pre-evacuated ampoules as a function of capillary diameter for 3 compounds (consecutive flow conditions: Knudsen diffusion, super sonic, turbulent, laminar).

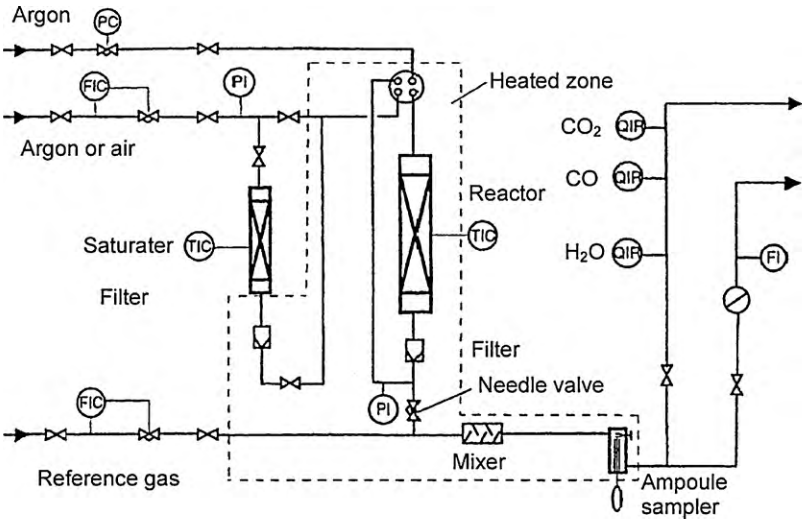


Fig. 3. Apparatus for time resolved investigation of methanol conversion on zeolite catalysts, (*) methanol saturator to provide a distinct methanol partial pressure, avoiding any fluctuations, (*) reference gas (neopentane + nitrogen) for quantitative GC-analysis to determine directly yields and selectivities, (*) reactor: inserted fused silica reactor tube, bed of zeolite crystallites layer on fused silica particles, (*) ampoule sampling after depressurizing and admixing the reference-gas flow, (*) on-line analysis of CO_2, CO, H_2O for use during TPO.

The gas chromatograph was adapted for ampoule samples (heated ampoule breaker in the carrier gas line). This sampling method was also used for time resolved analysis of the desorbed compounds during TPD of used catalysts.

The flow sheet of the apparatus for methanol conversion is shown in Fig. 3 [24–25]. Specific features are: (1) internal reference for time resolution by admixing a reference-gas stream (2,2-dimethylpropane in nitrogen) to the product-gas stream. The 2,2-dimethylpropane-peak in the chromatograms is used as reference for yields and selectivities. (2) Feeding of methanol to the reactor, without any fluctuation, at a rate of only ca. 1 g/h was achieved by vaporizing methanol into an argon stream with a vaporizer loaded with porous ceramic particles, these wetted with methanol. The vaporizer was held at the right temperature to obtain the desired methanol vapor pressure. The molar ratio of methanol to argon was kept as one, the total pressure at 5 bar, WHSV was 1. (3) The reactor tube of fused silica was inserted in a steel jacket. The catalyst bed consisted of 0.5 g zeolite crystallites diluted with coarse silica spheres (0.2–0.4 mm diameter, weight ratio 1:10) for uniform flow at negligible pressure drop and isothermal operation. The zeolite crystallites were deposited as a homogeneous layer on the surface of the fused silica spheres. (4) For ampoule sampling from the reactor effluent, evacuated ampoules were inserted with their capillary end into the product stream; the capillary end was broken, the ampoule representatively filled in less than 1 s, the ampoule sealed at the capillary end with a little flame and the ampoule stored for later GC-analysis. (5) At zero time, the flow to the reactor was switched from the argon bypass to the adjusted feed flow. (6) Constant reaction pressure was attained by admixing a pressure-controlled argon flow to the product flow before the depressurizing needle valve.

The same apparatus was used for temperature programmed desorption (TPD) and oxidation (TPO) of catalysts after use for methanol conversion. During TPD, ampoule samples of the product gas were taken for gas chromatographic analysis. On this basis distinct decomposition reactions of the retained organic matter could be discriminated. Quantitative TPO data were obtained by monitoring continuously CO_2, CO and H_2O in the effluent gas.

Zeolite H-ZSM-5 as catalyst was applied in a wide range of reaction temperature (270–475 °C). For understanding the mechanism on H-ZSM-5 in relation to its pore architecture, the wide pore zeolite H-Y was used also. Additionally, the conversion of methanol on the zeolites H-ZSM-58, H-EU-1 and H-Beta was studied, their coking behavior being explained on the insight obtained with the zeolites H-ZSM-5 and H-Y. Data about the pore architecture of the used zeolites are shown in Fig. 4 and Table 1 [24,26]. For discussing spatial constraints, the size of cavities (to allow distinct transition states and to host big molecules) and the diameter of channels (to allow diffusion in the pore system) are noticed. Similar experimental techniques have been used for investigating self-organization in Fischer-Tropsch synthesis on iron and cobalt catalysts [27,28].

3. Evaluation of results from the primary data

For discussing results, particular diagrams have been chosen. *Methanol conversion at low temperature:*

(1) Yields of volatile compounds and retained organic matter as depending on time-on-stream with zeolite H-ZSM-5. This diagram characterizes the regimes (see below)—of first reactions

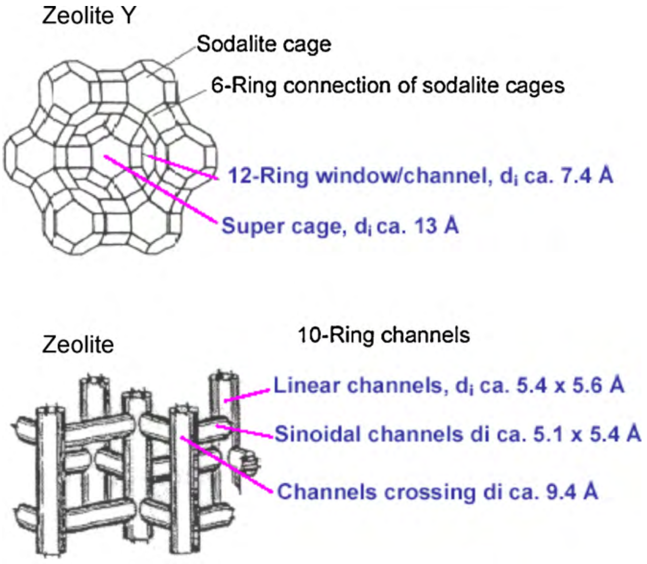


Fig. 4. Structures of zeolites Y and ZSM-5.

Table 1
Zeolites used as catalysts for methanol conversion.

Zeolite	Cage/crossing (Å)	Channels (Å)	Pore system	Si/Al molar	Ref.
Y	13	12-Ring 7.4	3-Dimensional	5	[2]
ZSM-5	9.4	10-Ring 5.1 × 5.5 5.3 × 5.6	2-Dimensional linked	100	[1]
ZSM-58	ca. 7	8-Ring 3.6 × 4.4	3-Dimensional	30	[3]
EU-1	6.8 × 5.8 × 8.1(6 8 × 5.8 × 13)	10-Ring 4.1 × 5.7	1-Dimensional with side-pockets	20	[3]
Beta	ca. 10	12-Ring 7.6 × 6.4 5.5 × 5.5	3-Dimensional	35	[2]

Zeolite samples kindly supplied by (1) C.I. O'Connor, Cape Town, RSA, (2) Z. Yien, Fushun, PR China and (3) J. Weitkamp, Stuttgart, Germany.

(incubation), fast increase of rate (autocatalysis) and retarding (inhibition through accumulation of organic compounds).

(2) Selectivity of methane in the incubation period (indicating dehydrogenation by methanol).
(3) Selectivity of retained organic matter in dependence of temperature with H-ZSM-5 (indicating deactivation to decrease with increasing temperature).
(4) Composition of thermally desorbed compounds from at 270–300 °C used zeolite H-ZSM-5 as a function of desorption temperature (indicating structures of retained organic compounds).

Methanol conversion at high temperature (475 °C):

(5) Group selectivities ("coke", methane, paraffins C_2+, aromatics, olefins) in dependence of time-on-stream. The time axis is normalized for comparing the deactivation behavior of different types of zeolites, the pattern of these diagrams characterizes the influences of shape selectivity.

4. General results of methanol conversion with the different zeolites

In Table 2 general results of methanol conversion on the five zeolites at 475 °C are presented [24]. With H-ZSM-5, catalyst life time is about 70 times longer than with the other zeolites. (Definition of life time: time-on-stream at break-through of methanol at the catalyst-bed end.) 123 g of methanol per gram of catalyst were processed with H-ZSM-5 but only about 2 g with the other zeolites. "Coke" on the deactivated catalysts was determined by TPD and TPO (temperature programmed desorption and oxidation). Only a small fraction of "coke" was removed by TPD from the catalysts used at high temperature. The amount of "coke" on the catalysts was calculated as carbon retained by recording the ingoing and outgoing carbon streams during methanol conversion. These values, called "by balance", are in reasonable agreement with values measured by TPD and TPO, except for H-ZSM-5 where coke selectivity is very low. During the long life time with H-ZSM-5, a similar amount of coke accumulates on the catalyst until deactivation as with the other zeolites during their short life time. As a peculiarity, the H/C atomic ratio is remarkably high with zeolite H-ZSM-58, the catalyst with narrow 8-ring channels. Apparently, the pore architecture of the zeolite H-ZSM-5 with 10-ring channels of ca. 5.5 Å diameter and cavities (channel crossings) of ca. 9.4 Å diameter is very unique in suppressing coke formation. It is an objective of this study to elucidate spatial constraints in the reaction mechanisms of methanol conversion on zeolites.

Photographs of the H-ZSM-5 catalyst after use for methanol conversion at low and high temperature have been taken. The fused silica tube with the catalyst was removed from the reactor. Fig. 5 shows photos of the catalyst bed after reaction at 475 and 300 °C. The low temperature deactivated catalyst had attained a yellow color which changed to pink after access of air. The color indicates highly unsaturated organic compounds. The catalyst from methanol conversion at 475 °C was taken from the reactor at about 15% life time. A black zone (of deactivated catalyst), a grey zone (of main methanol conversion) and a zone of light-blue color – in front of the reaction zone – can be distinguished. It is concluded, that in the front zone the catalyst is still active, but on external sites some "coke seeds" have been formed.

Evidently, the deactivating material is completely different at low and high temperatures. At high temperature a black coke phase apparently covers catalyst particles and the blue color further down-stream is suggested to refer to minor coking from olefins, no more methanol being present in this zone. At low temperature, unsaturated organic compounds are proposed to fill the pores (referring to the high average selectivity of retained organic matter of ca. 30 C-%).

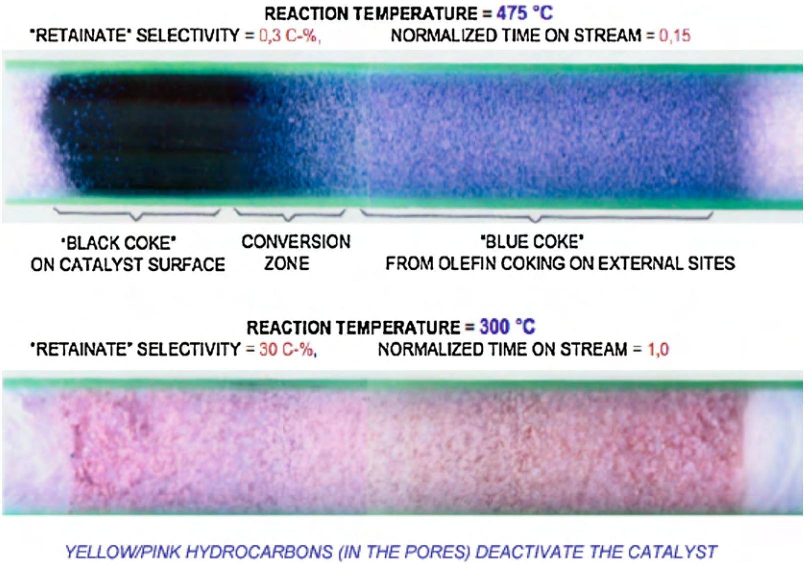
5. Low temperature methanol conversion on zeolite H-ZSM-5

Methanol conversion has been studied in the range 270–300 °C [29,30]. Ampoule sampling was applied for time resolution. Fig. 6 shows the yields of volatiles (sum of all organic compounds in the gaseous product stream) and of retained matter on the catalyst as a function of time at 270 °C.

Table 2
General data (life time, coke on catalyst by TPD and TPO, H/C-ratio of coke) about methanol conversion at 475 °C with the zeolites used as catalysts in this investigation.

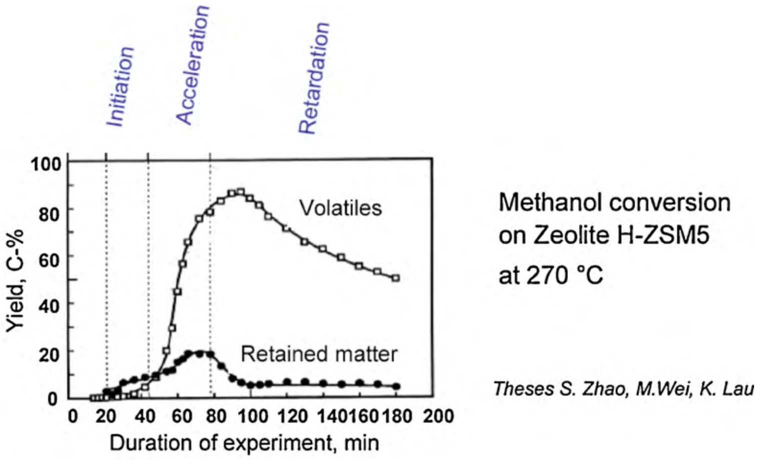
Zeolite	Life time (min)	A_{MeOH} (g/g)	"Coke" on catalyst				TOS (min)
			By balance (g/g)	TPD + TPO (g/g)	TPD (%)	H/C (molar)	
Y	116	1.9	0.32	0.26	(2.5)	0.8	190
ZSM-5	**7400**	**123**		0.25	(8.6)	0.8	8320
ZSM-58	95	1.6	0.17	0.14	(4)	1.4	180
EU-1	131	2.2	0.11	0.15	(5)	0.8	200
Beta	107	1.8	0.18	0.16	(14)	0.8	180

A_{MeOH}: amount of methanol processed at life time per gram of zeolite catalyst [g/g].



YELLOW/PINK HYDROCARBONS (IN THE PORES) DEACTIVATE THE CATALYST

Fig. 5. Photographs of the H-ZSM-5 catalyst bed after methanol conversion at high (above) and low (below) temperature.



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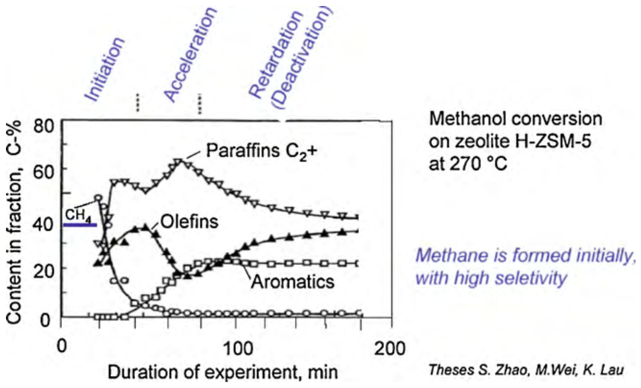
Initially, retained organic matter is obtained in higher yield than volatiles,
Causing autocatalysis
Later, "Retainate" fills the pores causing acceleration and then deactivation

Fig. 6. Yield of products (volatiles and retainate) as function of time-on-stream for methanol conversion on H-ZSM-5 at low temperature.

During the first 20 min "no" volatile hydrocarbons are observed. During the next 20 min first volatile hydrocarbons are noticed. Remarkably, the mass balance indicates that during this period the yield of retained matter on the catalyst is even higher than the yield of volatiles (regime of initiation). From 40 to 80 min – after some organic matter has accumulated on the catalyst – the yields of volatiles and retained matter increase drastically (regime of acceleration/autocatalysis). It is concluded that the retained compounds in the zeolite pores play an essential role by reacting easily with methanol. But then the increasing amount of retained matter causes inhibition for reaction and diffusion (regime of deactivation/retardation).

The composition of the volatile product at 270 °C reaction temperature, as grouped for paraffins, olefins, aromatics and methane, is shown as a function of time in Fig. 7. An interesting result is the initially high selectivity of methane. This clearly corresponds to dehydrogenation of the retained compounds (the strongly unsaturated yellow molecules). The dehydrogenation reaction with methanol (CH_4 as co-product) is visualized in Fig. 8.



Methane is formed initially, with high seletivity

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Fig. 7. Composition of the volatile products as depending on time-on-stream during methanol conversion on zeolite H-ZSM-5 at low temperature.

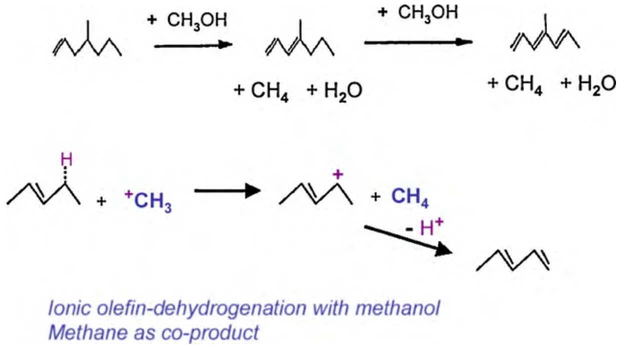


Fig. 8. Proposed mechanism of dehydrogenation of olefins with methanol, as relevant in the initiation regime of methanol conversion on zeolite H-ZSM-5 at low temperature.

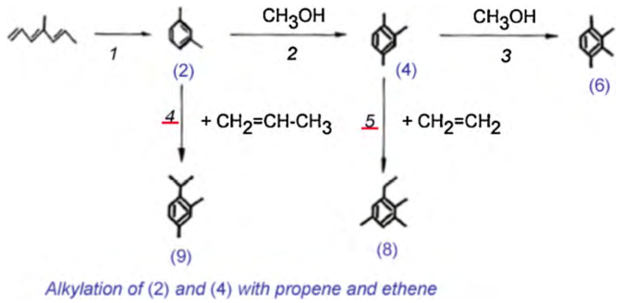


Fig. 9. Proposed mechanism (reactions) of formation of formation of molecules retained in the pores of zeolite H-ZSM-5 during methanol conversion at low temperature (270–300 °C).

5.1. Isolation of retained compounds [25,31]

Samples of at low temperature deactivated catalyst were treated with fluoric acid for dissolving the zeolite, this followed by extraction with CCl$_4$ of the organic retained matter which was analyzed by GC/MS (Table 3). It is noticed that the retained matter from the catalyst after 60 min time-on-stream consists predominantly of the compounds 1-ethyl,2,3,5-trimethylbenzene (8) and 1-isopropyl,2,4-dimethylbenzene (9). It is concluded, that the transition states for these compounds – formed very probably by alkylation of the benzene ring with the olefins ethene and propene – still finds space in the ZSM-5 cavities, however, their size being too big for diffusing through the channels. The visualized alkylation reactions are shown in Fig. 9.

5.2. Thermal regeneration

Table 4
Thermal regeneration of H-ZSM-5 after methanol conversion at low temperature.

Temperature of methanol conversion, °C	270	290
Time-on-stream, min	180	180
Temperature of maximal desorption rate, °C	310	340
"Retainate" desorbed: (TPD), g/g	0.053	0.037
TPO (after TPD), g/g	**0.000**	0.003
Composition		
$C_{aromatic}/C_{aliphatic}$, g/g	0.64	0.79
H/C, molar ratio	1.68	1.64

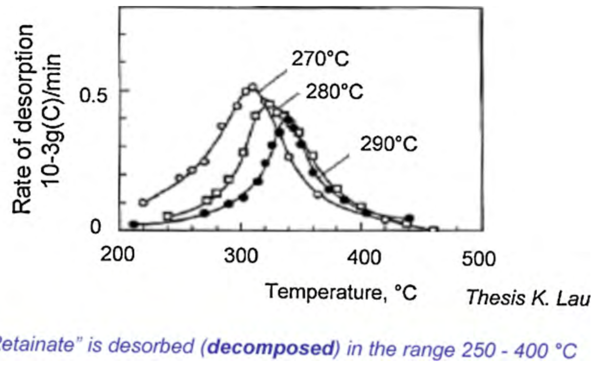
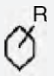
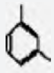
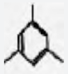
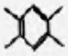
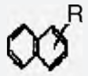


Fig. 10. TPD of H-ZSM-5 after methanol conversion at 270, 280 and 290 °C.

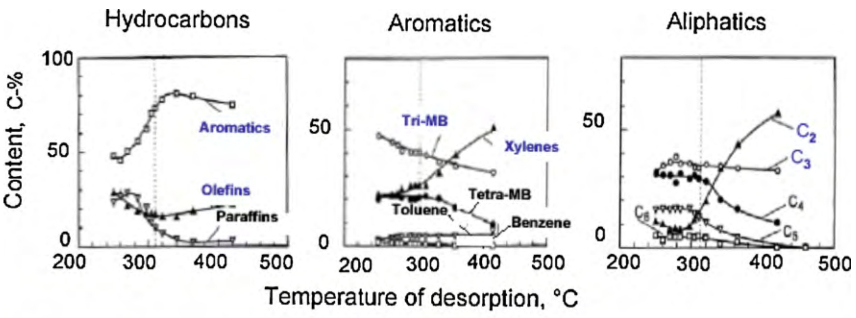
For characterizing the low reaction temperature on zeolite H-ZSM-5 retained organic matter, TPD and TPO of the used catalyst were applied [24,29]. Results are shown in Table 4 and Figs. 10 and 11. The temperatures of maximal desorption-(decomposition-) rate of retained matter are 310 and 340 °C for the catalysts used at 270 and 290 °C, respectively. TPO after TPD shows only small amounts of carbon left on the catalyst after thermal treatment. This means that "real coke" (coke being a black carbon-rich phase—not a molecule) is not present. The "retainate" from slightly higher reaction temperature (290 °C) is of more aromatic nature ($C_{aromatic}/C_{aliphatic} = 0.79$, molar H/C-ratio = 1.64,) than retainate from lower reaction temperature (see Table 4).

The ampoule samples of the effluent gas from TPD were analyzed by gas chromatography. The results are presented in Fig. 11 for the catalyst used at 270 °C. The "desorbed" compounds are mainly aromatics and olefins. Among the aromatics at TPD temperature, above 320 °C, xylenes and trimethylbezenes – and among the aliphatics ethene and propene – are dominating. It follows, the release of retained matter during TPD corresponds to the decomposition of alkylated benzene molecules, and more specifically, to dealkylation of those kind of aromatic compounds which mainly have been isolated from used catalysts—1-ethyl,2,3,5-trimethylbenzene (8) and 1-isopropyl,2,4-dimethylbenzene (9) (see Table 3) as pictured in Fig. 12. The TPD results support low temperature deactivation of H-ZSM-5 during methanol conversion to proceed through alkylation of benzene rings with ethene and propene. At higher temperature this reaction will be reversible and no longer deactivating. This explains how with increasing reaction temperature, catalyst life time increases and "retainate" yield decreases from ca. 10% at 290 °C to only ca. 0.3 C-% at ca. 380 °C

Table 3
Isolated "retainate" compounds from H-ZSM-5 after methanol conversion at 270 °C.

Time-on-stream (min)	 (1)	 (2)	 (3)	 (4)	 (5)	 (6)	 (7)	 (8)	 (9)	 (10)
22	2	3	4	**10**	1	**21**	5	**36**	2	**16**
36	6	2	**1**	16	3	10	14	27	9	12
60	5	1	**1**	3	10	13	8	**28**	**24**	7

GC–MS analysis, composition in C-%.



Thermal regeneration refers to dealkylation of aromatics

Fig. 11. Composition of the fractions of “hydrocarbons”, aromatics” and “aliphatics” as a function of desorption temperature during TPD of a H-ZSM-5 catalyst after use at 270 °C for methanol conversion (analysis of TPD effluent gas by GC of ampoule samples).

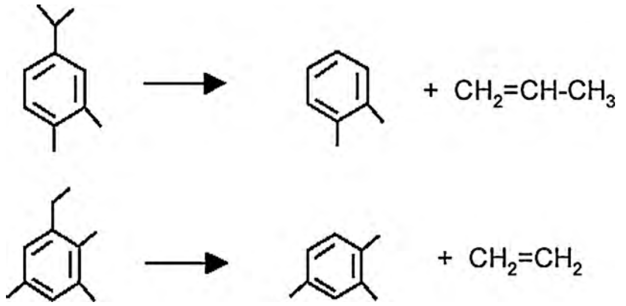


Fig. 12. Proposed mechanism (reactions) of thermal H-ZSM-5 regeneration/reactivation (after use for methanol conversion at low temperature).

(Fig. 13, [32]). Decreasing deactivation at increasing reaction temperature is very peculiar, it can be attributed to the specific pore system of zeolite H-ZSM-5. The term “reanimation” has been proposed for this special kinetic regime of reactivation [29].

It is seen in Fig. 13 also that at reaction temperatures higher than 400 °C, catalyst life time decreases and yield of retained matter increases as normally observed for coking. Obviously, the mechanism of deactivation changes.

The high temperature deactivated catalyst can be only regenerated by oxidation (see Fig. 5).

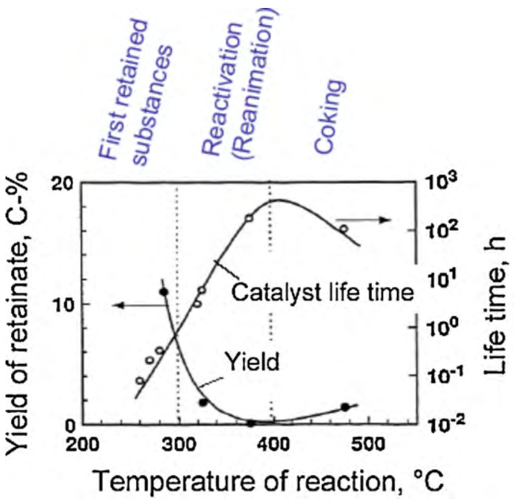


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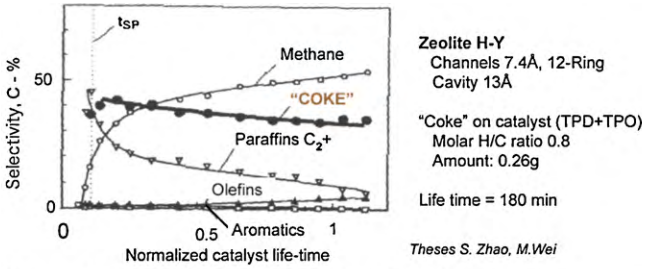
Fig. 13. Catalyst life time and yield of retained matter (“retainate”) as a function of reaction temperature in methanol conversion on zeolite H-ZSM-5.

6. Methanol conversion at high temperature on several zeolite catalysts

Catalyst deactivation at high temperature methanol conversion (475 °C) has been studied with several zeolites in order to elucidate the mechanistic impact of spatial constraints of different zeolite structures. The course of reaction on the wide pore zeolite H-Y is regarded in comparison with conversion on zeolite H-ZSM-5. The results are presented in diagrams of selectivity over normalized life time. At normalized life time one, the break-through of methanol at the catalyst-bed end is noticed. The normalized abscissa is suited for comparing deactivation of different zeolites. Selectivity of the multi-compound product is grouped for olefins, aromatics, paraffins C_2+, methane and “coke”. The composition of the gas phase has been determined by gas chromatography of ampoule samples. The yield of coke was calculated as mass balance difference of carbon from reactor ingoing and outgoing streams.

7. Deactivation of zeolite H-Y

Zeolite H-Y deactivation proceeds with high coke selectivity of ca. 40 C-% (Fig. 14). Obviously, the pores of this zeolite are readily filled with deactivating matter. “No” volatile aromatic compounds are obtained. It is assumed that mono-ring aromatics, which are obtained with zeolite H-ZSM-5, are converted to bigger retained molecules in the pores of zeolite H-Y. Almost no olefins are observed: these primary products, obviously, react further. Initially, volatile paraffins C_2+ are the hydrogen-rich co-product to the hydrogen-deficient coke. This is assigned to hydride transfer occurring initially abundantly. Towards normalized time one, the selectivity changes to methane being the hydrogen-rich co-



Life-time (t_{LIFE}) = Time-on-stream at methanol break-through at bed end

$$\text{Normalized life-time } (t_{LIFE,NORM}) = \frac{\text{Time on stream}}{\text{Life-time}}$$

Initially paraffins and “coke” (extensive hydrogen transfer)
finally methane and “coke” (only methylation and dehydrogenation by methanol

Fig. 14. Deactivation pattern of zeolite H-Y during methanol conversion at 475 °C. Group selectivities (methane, olefins, paraffins C_2+, aromatics, “coke”) as a function of normalized catalyst life time.

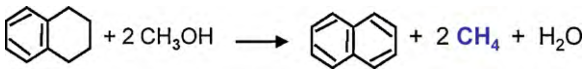
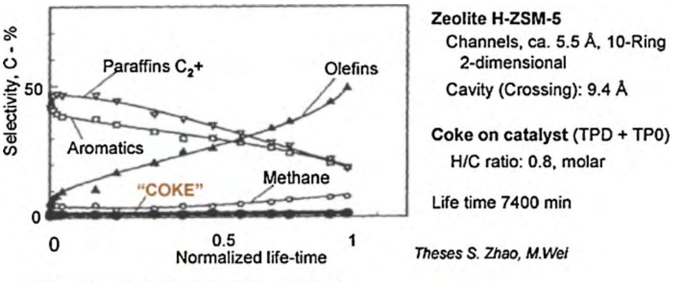


Fig. 15. Principle of "retainate"- (coke-) dehydrogenation with methanol (as simple coke-model for this reaction tetralin has been taken).



Very low coke selectivity (no pore filling)
Increasing methane selectivity (Coke growth on surface)
Initially: Hydrogen transfer; Finally: Olefins dominate

Fig. 16. Deactivation pattern of zeolite H-ZSM-5 during methanol conversion at 475 °C (see legend of Fig. 14 for further explanation).

product to the hydrogen-deficient "coke". In this regime, "coke" and methane are the only products. The mechanism is then visualized as the retained matter ("coke") to grow by methylation with methanol and to be dehydrogenated by reaction with methanol, with CH_4 and H_2O as co-products.

With zeolite H-Y at 475 °C, the retained matter in the pores might consist mainly of 2-ring, respectively, 3-ring compounds, still being reactive for methylation and dehydrogenation. Dehydrogenation is pictured in Fig. 15.

8. Deactivation of zeolite H-ZSM-5

The pattern of zeolite H-ZSM-5 deactivation at 475 °C is shown in Fig. 16. "Coke" selectivity is less than 1 C-%, indicating pore filling not to proceed. This corresponds to the "reanimation principle" that the biggest molecules which can be formed in the cavities via alkylation of benzene rings with ethene or propene are instable against dealkylation.

Initially, aromatics (benzene derivatives) and paraffins C_2+ are obtained. This reflects exhaustive hydrogen transfer. With ongoing deactivation, olefins dominate in the product, as being primary products. Finally, methane selectivity increases to about 10 C-%, indicating dehydrogenation of "coke" (on the surface) with methanol (Fig. 17).

8.1. Zone ageing of H-ZSM-5 at 475 °C

Changes of product composition with time will also depend on the kind of reactor. In Fig. 18 a photograph of the catalyst in the reactor tube, after interruption of conversion at about 15% normalized life time, is shown. Apparently, there is the black zone of deactivated catalyst (with coke on the surface), then a grey reaction zone (where most of the methanol is converted) and in front a light-blue zone (which is assigned particularly to olefin reactions, these including formation of "coke seeds" on the surface, in addition to reacting to aromatics and paraffins. The reaction zone migrates slowly along the catalyst bed.

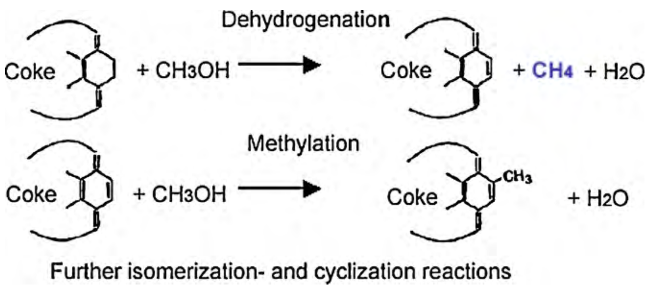
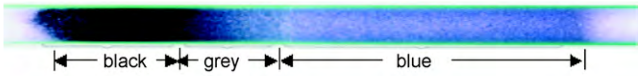


Fig. 17. Proposed reactions of "coke growth" on the surface of zeolite H-ZSM-5 crystallites, methanol conversion at 475 °C.



Zones of catalyst bed:
Black External coked, deactivated, *(continuing coke growth with method)*
Grey Reaction zone (MTO)
Blue Active catalyst (Coke seeds on surface from olefin reactions)

Fig. 18. Zone ageing of zeolite H-ZSM-5, methanol conversion at 475 °C.

8.2. Issues about MTO reactors with zeolite H-ZSM-5 would be

8.2.1. Fixed bed

Undesirable reactions proceed in front- and tail-zone; formation of paraffins and aromatics from olefins in the front zone and formation of further coke and methane by reaction of methanol with coke in the tail-zone.

8.2.2. Fluid bed

Fresh and old catalyst particles are mixed, resulting in further coke- and methane formation on old catalyst and formation of aromatics and paraffins from olefins on fresh catalyst.

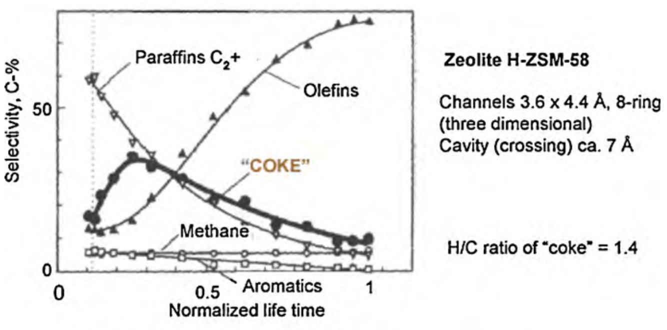
8.2.3. Moving bed

Catalyst bed length can equal the reaction zone length: less coke, methane, aromatics and paraffins are formed.

As deactivation of H-ZSM-5 during methanol conversion at high temperature, evidently, proceeds via coke formation on the catalyst surface, particle size and particle density and kind of active sites on the crystallite surface will be of influence on catalyst life time. Such influence of particle size on catalyst life time (at 400 °C during methanol conversion has recently been reported [33]. It is generally suggested for future work to measure selectivity as a function of time (as shown in this article) for tracing catalyst deactivation and guiding catalyst development.

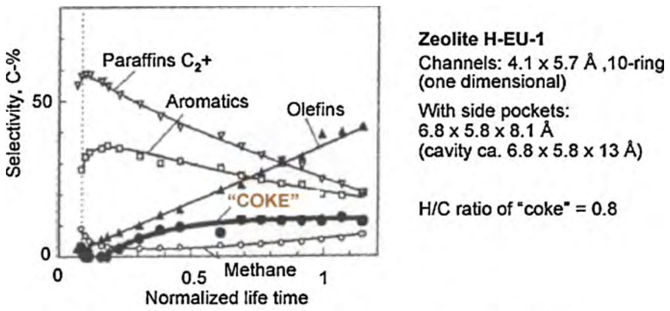
9. Deactivation of zeolite H-ZSM-58

Selectivity during deactivation of zeolite H-ZSM-58 is shown in Fig. 19 [24]. There are merely aromatics among the volatile products. A high selectivity of "coke" indicates pore filling reac-



Initially paraffins and "coke", then olefins
High H/C-ratio of "coke" corresponds to tetramethyl-benzene

Fig. 19. Deactivation pattern of zeolite H-ZSM-58, methanol conversion at 475 °C.



Initially, paraffins and aromatics; then, increasing coke selectivity (pockets being presumably filled with aromatics like naphthalene)

Fig. 20. Deactivation pattern of zeolite H-EU-1, methanol conversion at 475 °C.

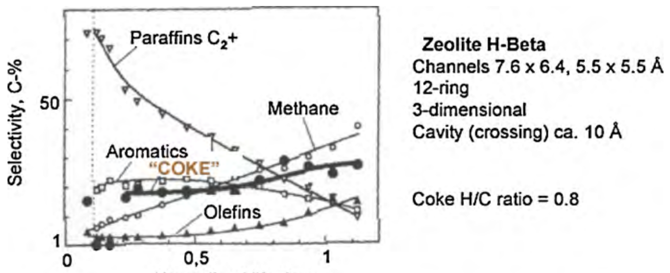
tions. The 8-ring channels are narrow (3.6 × 4.4 Å) as compared with zeolite ZSM-5 (ca. 5.5 Å), obviously these allowing no diffusion of benzene derivatives in the pore system. Cavities (channel crossings) are also smaller (ca. 7 Å) than in ZSM-5 (ca. 9.4 Å). It is anticipated that with this zeolite, benzene-ring formation is still possible in the cavities, however, channels being too narrow for diffusion of (methylated) benzene molecules. The high value of the H/C-ratio of the retained matter of 1.4 (corresponding to the H/C-ratio of tetramethylbenzene) supports this assumption. With ongoing deactivation, cyclization reactions in the cavities appear to be suppressed and olefins are the main product.

10. Deactivation of zeolite H-EU-1

Selectivity during deactivation of zeolite H-EU-1 is shown in Fig. 20. Initially, paraffins and aromatics are the main products referring to a similar conduct as with zeolite H-ZSM-5, however, then "coke" selectivity increases, probably because bigger aromatic molecules are formed and trapped in the side-pockets. The H/C-ratio of the retained matter corresponds to that of naphthalene.

11. Deactivation of zeolite H-Beta

Selectivity during zeolite H-Beta deactivation (Fig. 21) exhibits a mixed behavior. Both, volatile aromatics and "coke" are obtained. With ongoing deactivation, methane selectivity increases, indicating more dehydrogenation of "coke" by methanol. Comparing this behavior with that of zeolite H-Y, both zeolites having 12-ring channels but the cavity of zeolite Beta being smaller (ca. 10 Å as compared with 13 Å of Y-zeolite) it is suggested that the maximal size of aromatic molecules formed in zeolite Beta cavities is smaller, and their diffusion in the channels is possible to some extent.



Initial hydride transfer changes to final dehydrogenation with methanol.
Size of cavities allows trapping of aromatics.

Fig. 21. Deactivation pattern of zeolite H-Beta, methanol conversion at 475 °C.

There is an interesting pattern of aromatics selectivity during deactivation of zeolite H-Beta (Fig. 22, right). From initially mainly benzene, the composition changes to finally mainly hexamethylbenzene. This refers to initial formation of benzene and later to exhaustive benzene-ring methylation, the channels being sufficiently wide for diffusion of polymethylated 6-rings. With zeolite H-ZSM-5 the trend towards higher degree of methylation of benzene rings with time is also noticed (mainly in the beginning of the experiment (Fig. 22, left). The increasing degree of benzene methylation with time-on-stream might be explained by establishing the methanol reaction zone in the catalyst bed. When methanol enters the fresh catalyst bed, the reaction zone is short (all methanol being consumed, benzene being the main aromatic compound, obtained through cyclization without further methylation). The reaction zone spreads with time and methanol will be available over a broader section of bed length, leading to further methylation. With zeolite H-Beta the reaction zone is broader than with zeolite H-ZSM-5.

12. Basic reactions during methanol conversion on acidic zeolites

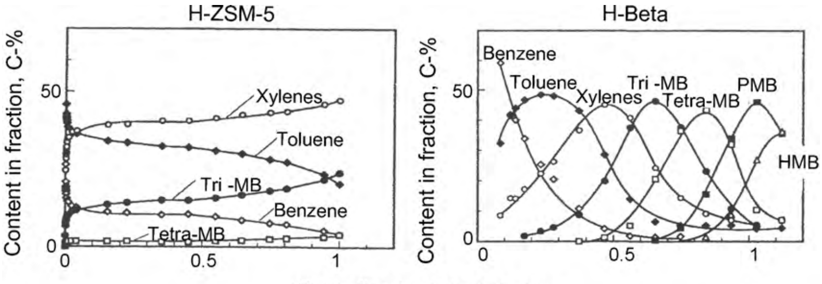
The reactions can be divided in two groups—reactions of methanol with hydrocarbons and reactions of hydrocarbons with each other. Among methanol reactions, methylation and dehydrogenation are distinguished.

12.1. Methanol reactions

12.1.1. Methylation (Table 5)

Methylation with methanol on the zeolites in their acidic (proton) form is visualized as attack of the methyl cat ion, the methyl cat ion being obtained by abstraction of OH^- from methanol with the proton of the catalyst ($CH_3OH + H^+ \Rightarrow CH_3{}^+ + H_2O$).

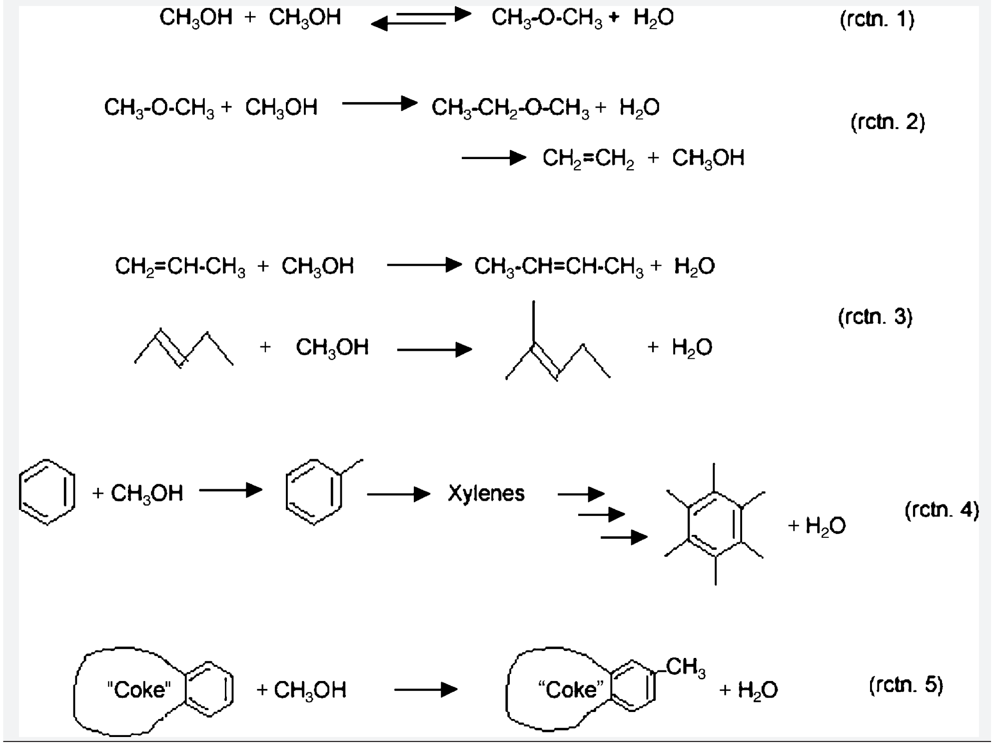
At low temperature, "first formation of hydrocarbons" (rctns. 1 and 2 in Table 5) are of interest (regime of initiation). After some hydrocarbons (olefins) have formed (in the pores) these react



Degree ofmethylation increases with time
With zeolite H-Beta: Initially benzene, finally hexamethyl-benzene is favored

Fig. 22. Aromatics composition as function of normalized life time for the zeolites H-ZSM-5 and H-Beta during methanol conversion at 475 °C.

Table 5
Proposed methylation reactions of methanol during methanol conversion on acidic zeolites.



fast with methanol (rctn. 3). Methylation of aromatic rings with methanol may perform persistently (rctns. 4 and 5), however, not extensively with zeolite H-ZSM-5.

Methylation with methanol appears to be essential in “coke growth” during H-ZSM-5 deactivation. As coke being an amorphous carbon-rich phase and not a molecule, the term “coke growth” is being used.

12.1.2. Dehydrogenation of hydrocarbons (Table 6)

Dehydrogenation with methanol is visualized to proceed via hydride transfer, leading to polyenes from olefins (rctn. 1), to aromatics from cycloalkenes (rctn. 2) and to higher aromaticity of “coke” (rctn. 3), methane being the indicative co-product of this reaction.

12.2. Reactions of hydrocarbons with each other

Hydrocarbon reactions (carbenium ion reactions) during methanol conversion on acidic zeolites are pictured in Table 7. The alkylation/dealkylation equilibrium of benzene and benzene derivatives with ethene and propene (rctns. 1 and 2) is on the dealkylation side at the temperatures of the MTG and MTO processes (above 350 °C) (as shown by the TPD experiments, see above).

Table 6
Proposed dehydrogenation reactions of methanol during methanol conversion on acidic zeolites.

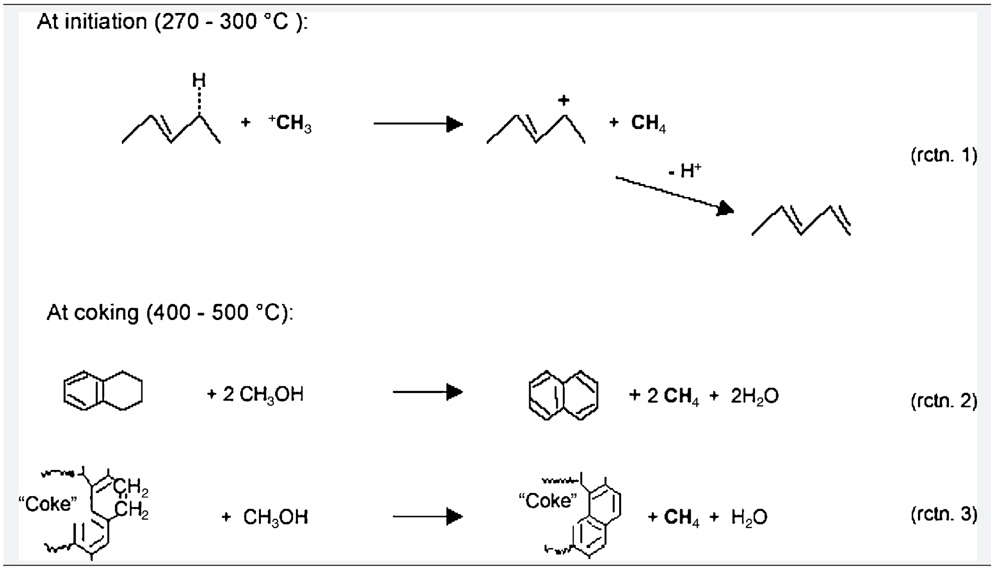
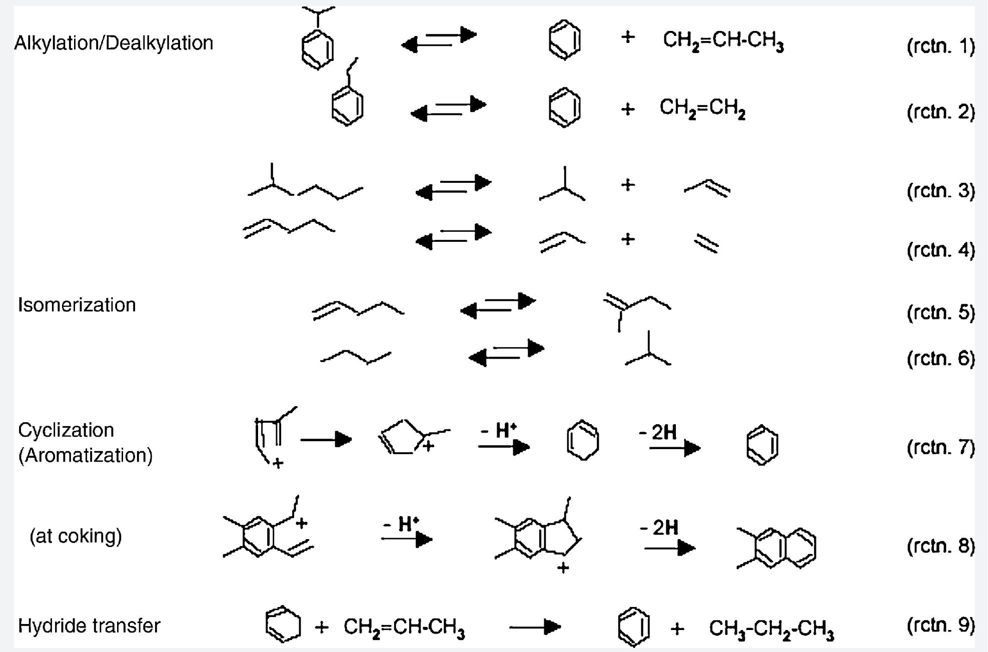


Table 7
Hydrocarbon reactions during methanol conversion on zeolite H-ZSM-5 (and on further zeolites).



Similarly, alkylation/dealkylation of olefins can be regarded to be on the side of small molecules as propene and ethene at high temperature (rctns. 3 and 4).

Cyclization and aromatization (hydride transfer) – pictured as rctns. 7 and 9 – can easily proceed (as pertinent from various product compositions, see above) if not suppressed by spatial constraints. The same applies for "coke"—(retained matter, respectively, retained molecules) formation.

Spatial constraints on transition states with zeolite H-ZSM-5, evidently, allow as biggest molecules to form only one-ring aromatics. Whether they can diffuse through the channels depends on kind and degree of alkylation. As supported by this investigation, methylation with methanol is not exhaustive and only methylated 6-rings which can diffuse in the pore system are formed. However, alkylation of the benzene ring with ethene and propene, which are constituents of the reaction mixture in the pores, leads to compounds which are trapped. At higher reaction temperature (above 300 °C) these compounds decompose (dealkylate) and do no more block the pore system. Coking of zeolite H-ZSM-5 during the methanol to olefin conversion, obviously, does not proceed in the pores but on the crystallites surface, as early suggested by Bibby et al. [34]. As follows from this investigation, it proceeds via methylation and dehydrogenation for coke growth by reaction with methanol.

Table 8
Tentative comparison of aspects of MTO processes.

	MTP (Lurgi)	MTO (UOP/Hydro)
Catalyst	H-ZSM-5	H-SAPO-34
Channels	10-Ring (5.5 Å)	8-Ring (3.8 Å)
Cavity (crossing)	~9.4 Å	~6 Å
Temperature, °C	450	350
Pressure, bar	1.5	2
Reactor	Fixed bed	Fluid bed
Recycle	Water, olefins C_4+, C_2	–
Products, wt%[a]		
Propene	72	42
Ethene	–	39
C_5+	23	5

[a] Composition can vary.

In order to increase olefin selectivity, the (secondary) formation of aromatics should be suppressed (dilution with H_2O, favorable reactor design, appropriate reaction conditions favorable catalyst design). Propene selectivity would be increased by recycling of olefins C_4+. Some data of industrial processes for olefin production from methanol have been published (Table 8, [20,21]). It appears that spatial constraints interfere mechanistically in a different way with H-SAPO-34 as compared with zeolite H-ZSM-5.

13. Conclusions

Selectivity of methanol conversion on zeolite H-ZSM-5 is observed to change with time—the retained matter on the catalyst playing an essential role. At low temperature (270–300 °C), first hydrocarbons in the pores react mainly to retained bigger unsaturated compounds by methylation and dehydrogenation with methanol. The reaction rate increases drastically (mechanistic regimes of initiation and acceleration). By alkylation with ethene and propene (as concluded from TPD-selectivity with used catalysts and from isolation of deactivating matter) ethyl-trimethyl-benzene and isopropyl-dimethyl-benzene are formed, being the mayor retained compounds blocking the pore system and deactivating the catalyst at low temperature.

At higher temperature (300–400 °C), alkylation of benzene rings with olefins is reversible, and the ZSM-5 catalyst is reactivated ("reanimated"). Accordingly, at the temperature of the MTO conversion on H-ZSM-5 (e.g. 450 °C), deactivating pore filling does not proceed. Coke formation on the surface of the H-ZSM-5 crystallites is slow, initially on "coke seeds" from olefin-coking (down-stream before the methanol reaction zone). By further reaction of coke with methanol for methylation and dehydrogenation, the catalyst is deactivated. Methane among the volatile compounds is indicative for this kind of coking. Spatial constraints in the cavities of H-ZSM-5, evidently, control the size of formed aromatic (alkylated) mono-ring compounds. Dealkylation of ethyl- and isopropyl groups from benzene rings is in equilibrium with alkylation as depending on temperature. The modestly methylated 6-ring aromatics diffuse through the channels.

In a fixed bed of H-ZSM-5 catalyst, the reaction zone migrates slowly. Before and behind the reaction zone undesirable reactions proceed, as there are further coke growth on the deactivated catalyst – associated by methane formation – and formation of aromatics and paraffins C_2+ aromatics via hydride transfer from olefins in the front zone before the methanol reaction zone. A moving bed reactor might exhibit favorable performance.

The improved understanding of spatial constraints in the pore architecture of zeolite H-ZSM-5 benefits from learning about the course of methanol conversion on (wide pore) zeolite H-Y. The H-Y-catalyst is soon deactivated by fast accumulation of “coke” in the pores (ca. 40 C-% coke selectivity). Finally, the deactivated H-Y zeolite continues to react with methanol, but only for “growth of coke”, methane being the co-product.

The course of deactivation of the zeolites H-ZSM-58, H-EU-1 and H-Beta – as ruled by their spatial constraints – is explained on the basis of reaction principles attained with the zeolites H-ZSM-5 and H-Y.

A general philosophy is in line with this study:

”The higher the complexity of the reaction product composition, the more inherent information will be provided” about catalytic sites, basic reactions, reaction intermediates and spatial constraints, this even the more when complexity varies with time, as in unsteady regimes like autocatalysis, self-organization or catalyst deactivation—however, availability of the right experimental methods is essential.

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