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Journal:	*Catalysis Letters*
Manuscript ID	CATLET-2016-0434.R1
Manuscript Type:	Original Manuscript
Date Submitted by the Author:	06-Sep-2016
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Keywords:	Heterogeneous catalysis < Catalysis, Deactivation < Elementary Kinetics, Acid catalysis < Processes and Reactions, CO hydrogenation < Processes and Reactions, Dehydration < Processes and Reactions, DME < Processes and Reactions, Bifunctionality < Elementary Kinetics

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Catalyst Deactivation during One-step Dimethyl Ether Synthesis from Synthesis Gas

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Abstract

Catalysts for direct synthesis of dimethyl ether (DME) from synthesis gas should essentially contain two functions, i.e. methanol synthesis and methanol dehydration. In the present work, the deactivation of both functions of hybrid catalysts during direct DME synthesis under industrially relevant conditions has been investigated with special focus on the influence of each reaction step on the deactivation of the catalyst function corresponding to the other step. A physical mixture of a Cu-Zn-based methanol synthesis catalyst and a ZSM-5 methanol dehydration catalyst was used. The metallic catalyst appears to deactivate due to Cu sintering, with no apparent effect from the methanol dehydration step under the conditions applied. The acid catalyst deactivates due to accumulation of hydrocarbon species formed in its pores. Synthesis gas composition, i.e. H_2/CO ratio and CO_2-content (which directly affects partial pressure of water), seems to influence the zeolite deactivation.

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Preprint submitted to Unknown Journal *April 13, 2016*

Keywords:
DME, methanol synthesis, methanol dehydration, deactivation, hybrid catalyst, H-ZSM-5, $Cu/ZnO/Al_2O_3$

1. Introduction

Dimethyl ether (DME) is a colorless, non-toxic gas that can be liquefied under moderate pressures. Earlier, DME was primarily used as an aerosol propellant, but its application has considerably grown over the recent decades as an LPG substitute or for LPG blending, especially in Asia [1–3]. DME is a fuel with high cetane number and clean burning properties that has the potential to replace diesel for use in compression ignition engines after implementation of slight modifications in the fuel injection system [4, 5]. Today, DME is mainly produced through a conventional two-step route, i.e. methanol synthesis from synthesis gas (mixture of H_2, CO and very often CO_2) over a Cu-Zn-based catalyst, followed by dehydration of methanol to DME over a solid acid catalyst. Alternatively, DME can be produced directly from synthesis gas over a hybrid catalyst capable of catalyzing both methanol synthesis and dehydration in a single step [6, 7]. The direct DME synthesis route is thermodynamically more favorable since syngas conversion to methanol is largely limited by thermodynamic equilibrium and further in situ conversion of methanol to DME shifts this equilibrium towards more methanol formation and allows for higher single-pass conversion of syngas.

Catalyst deactivation is an important aspect of any catalytic process. Deactivation of the hybrid direct DME synthesis catalysts may have its roots in deactivation of the methanol synthesis catalyst, the methanol dehydra-

tion catalyst or both, and may be caused by the well-known deactivation mechanisms corresponding to each reaction step or by specific deactivation modes originating from interactions between the two catalysts or the distinct reaction environment created by combining the two reaction steps in a single unit.

Methanol synthesis is a well-developed technology and despite the fact that catalyst deactivation has received less attention compared to other aspects of the process, there are still numerous theoretical and experimental studies concerning the matter, which have been extensively reviewed by several authors including Chinchen et al. [8], Kung [9], Twigg and Spencer [10, 11], and Bøgild-Hansen and Højlund-Nielsen [12]. During the first several decades of industrial-scale methanol production, with coal-derived synthesis gas as the feed, poisoning used to be the main concern regarding catalyst deactivation. Sulfur compounds, halogens and especially chlorine, transition metals such as Fe and Ni, alkali metals such as K and Cs, and arsine were identified as poisons for methanol synthesis catalysts [8–12]. The shift from coal to natural gas as the main source of synthesis gas in 1960s, along with improvements with regard to catalyst formulation, enabled the use of more active (but also more sensitive) Cu-based catalysts for methanol synthesis. Today, thanks to the advanced and efficient gas purification technologies, thermal sintering of copper is practically the only important mode of deactivation under normal operation in large-scale plants [10, 11]. The mechanism of thermal deactivation is a subject of an ongoing debate [13–15] and recent findings [16] suggests that additional mechanisms, e.g. disruption of the Cu-Zn synergy, may also play a role in catalyst deactivation. In order to

restrict the thermal deactivation, methanol synthesis is barely conducted at temperatures higher than or close to 300℃.

γ-alumina together with zeolites, especially ZSM-5, are the most widely applied solid acid catalysts for methanol dehydration to DME. Alumina is a rather stable catalyst but loses its activity very fast in the presence of H_2O, because of competitive water adsorption on the Lewis acid sites active for methanol dehydration [17–20]. Consequently, γ-alumina may not be suitable for conditions where the partial pressure of water is high, such as the use of crude methanol as the feed or for direct DME synthesis from CO_2-rich synthesis gas. In comparison, the activity of zeolites for methanol dehydration to DME is typically much higher and less susceptible to water inhibition [17, 18]. Zeolites, especially ZSM-5 and SAPO-34, are well-known catalysts for methanol conversion to hydrocarbons (MTH), and have been applied commercially in methanol-to-gasoline (MTG), -olefin (MTO) and -propylene (MTP) processes, where DME forms as an intermediate/byproduct in equilibrium with the methanol feed [21]. Methanol dehydration to DME over zeolites does not require the high temperature ($>$ 350℃) and long contact time which are essential for substantial hydrocarbon yield [22, 23].

Under typical MTH reaction conditions, coking is the well-known cause of zeolite deactivation [24]. Despite the wealth of information on deactivation under such conditions, in-depth investigation of H-ZSM-5 deactivation during DME synthesis, i.e. methanol dehydration under lower T and shorter contact time required to obtain high DME selectivity [23], is rather scarce. Nevertheless, investigations of the MTH reaction at low temperatures (260-300℃) by Schulz et al. [25–32] have provided valuable insights into the de-

activation mechanism of ZSM-5 during DME formation. According to their results, conversion of methanol/DME to hydrocarbons over ZSM-5 begins at a low rate with formation of unsaturated hydrocarbons, mainly retained inside catalyst pores, and co-production of methane. Subsequently, fast reactions of methanol with the retained hydrocarbons and the hydrocarbons with each other, intensify the hydrocarbon formation rate autocatalytically. Highly alkylated mono-ring arenes, especially ethyl-trimethyl-benzene and isopropyl-dimethyl-benzene, are the largest molecules that can form inside ZSM-5 pore system (channel intersections 9.4 Å) through alkylation of the benzene ring with light olefins, as demonstrated in Fig. 1. However, they are too big to diffuse out of the pores (channel openings of 5.1-5.6 Å). At high temperatures, benzene ring alkylation is reversible and the bulky alkylated benzene molecules break to smaller aromatics and olefins that can diffuse out of the ZSM-5 pores, but below 400℃, these molecules are rather stable and eventually deactivate ZSM-5 by filling the pores. Growth of hydrocarbons beyond bulky monocyclic arenes inside ZSM-5 pores is strongly restricted by spatial constraints, therefore, coke may only form on the outer surface of the ZSM-5 crystals [22, 30]. ZSM-5, owing to its three-dimensional 10-ring structure without trapping cavities, is much more resistant towards deactivation by coke compared to large pore zeolites with e.g. BEA, AFI, and CHA structures [18, 21]. Coking is favored by high temperatures ($>$ 400℃) and long contact times, and extensive coke formation can eventually deactivate the catalyst by blocking pore openings.

During direct DME synthesis, deactivation of methanol synthesis and methanol dehydration catalysts through the aforementioned mechanisms could

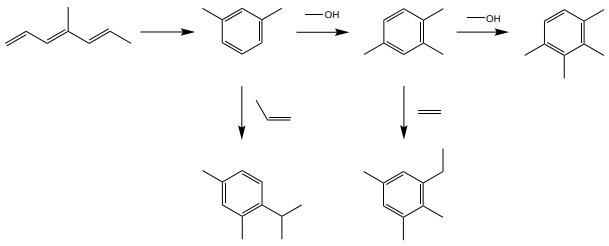

Figure 1: Irreversible alkylation of monocyclic aromatics leading to pore filling, proposed by Schulz et al. [31, 32] as the mechanism of ZSM-5 deactivation during methanol conversion at low temperature.

be affected by the distinct reaction atmosphere created by combining the two reactions. For instance, water and methanol are involved in both reaction steps and their concentrations in the reaction medium may differ from those of each separate step under otherwise similar conditions (T, P). Steam produces diverse effects on both functions of the catalyst, e.g. enhances the stability of Cu-Zn-based catalysts in low concentrations [33], assists Cu sintering [33–37] and disruption of the Cu-Zn synergy [16] at high partial pressures, hinders coke formation [20], deactivates γ-Al_2O_3 by strong adsorption [17–19], and reduces formation of deactivating carbonaceous compounds on H-ZSM-5 [18]. High partial pressure of methanol is also suggested to intensify Cu sintering [38]. Moreover, certain dehydration byproducts such as toluene, if present in large concentrations (500 ppm), can permanently deactivate the Cu-based catalyst through wax formation and pore filling [39]. Limited learning also exists from the literature concerning the effect of synthesis gas compositions on deactivation of the solid acid catalyst [40, 41].

Detrimental interactions between Cu-Zn-based methanol synthesis function and γ-Al_2O_3 [42] or ZSM-5 [37, 43–47] methanol dehydration function

have also been identified as a possible cause of deactivation. García-Trenco and Martínez reported a correlation between the concentration of extra-framework Al species (EFAl) on the ZSM-5 surface and deactivation of the hybrid catalyst, and concluded that the EFAl species may migrate onto the metallic catalyst through a water assisted mechanism, thereby disrupting the Cu-Zn synergy [45, 46]. On the other hand, García-Trenco et al. also suggested that Cu-Zn-based methanol synthesis catalyst contributes to ZSM-5 deactivation through partial blockage of zeolite pores as well as ion exchange of acidic H^+ by Cu^{2+} (and possibly also Zn^{2+}) [43]. Similarly, Ordomsky et al. contended that migration of Cu into the zeolite pores through a mechanism assisted by water and hydroxyls (Brønsted acid sites) on the outer surface of ZSM-5, and subsequent ion exchange between Cu^{2+} and acidic H^+ of the zeolite, deactivate both functions of the hybrid catalyst [37]. Peng et al. investigated the deactivation of a hybrid catalyst composed of a commercial methanol synthesis catalyst and γ-Al_2O_3 and suggested the migration of Cu- and Zn-containing species from the metallic to the acid catalyst as a cause of deactivation of both functions [42]. The preparation method of the hybrid catalyst is central to this deactivation mechanism as intimate solid-state contact between the two catalysts is necessary for such interactions to take place [37, 42–45]. According to the results reported by García-Trenco et al. [43–45], intimate contact of the two catalyst components does not seem to provide any enhancement in the catalytic performance, hence, in this study a mixture of pre-pelletized catalysts were used to prevent the adverse interactions between the two components.

The objective of the present work is to investigate catalyst deactiva-

tion during direct DME synthesis, with more focus on interactions between methanol formation and methanol dehydration. Cu-Zn-based methanol synthesis catalyst and ZSM-5 methanol dehydration catalyst were studied, first, under conditions corresponding to each reaction step and then under direct DME synthesis conditions. The operating conditions were chosen to be as representative of typical industrial conditions as possible, which is not always the case in the literature due to practical challenges involved with high methanol partial pressures. The common ambiguity in the literature regarding which reaction step controls the overall DME synthesis kinetics, was avoided.

2. Experimental

2.1. Catalysts and catalysts characterization

Two different commercial Cu/ZnO-based and one homemade Cu/ZnO/Al_2O_3 methanol synthesis catalysts were used throughout this study, which are referred to as CZ-C1, CZ-C2 and CZ-H, respectively. The homemade catalyst was prepared by conventional co-precipitation, where an aqueous solution of $Cu(NO_3)_2$, $Zn(NO_3)_2$ and $Al(NO_3)_3$ was precipitated with a sodium carbonate solution, through slowly adding the two to an aqueous solution of sodium acetate at 50℃ and pH of 7. The precipitates were then aged for 30 min, washed extensively with deionized water, dried over night at 120℃ and calcined at 400℃ for 2 h under flow of air. Prior to calcination, the Na-content of the precipitates was checked using ICP-MS and confirmed as below 90 ppm. ICP-MS also indicated the Cu/Zn/Al molar ratio of the resultant catalyst as 22/57/21 mol.%. Prior to introduction of synthesis gas,

CZ catalysts were reduced in situ under a flow of 3% H_2 in N_2 over a 9 h-long stepwise temperature increase, followed by 8 h dwell at 250℃.

The H-ZSM-5 methanol dehydration catalyst was prepared by calcination of NH_4-ZSM-5 (CBV 8014, Zeolyst Int., SiO_2/Al_2O_3=80) at 600℃ for 4 h. The acidity of the zeolite was manipulated through proton-sodium exchange by treating an aliquot of the H-ZSM-5 with a $NaNO_3$ 0.05 M solution at 80℃, followed by washing with deionized water, overnight drying at 100℃ and calcining at 600℃ for 4 h. The Na/Al atomic ratio of the NaH-ZSM-5 was 0.12 as determined by ICP-MS and the acidity was 10% lower than the parent zeolite as measured by NH_3-TPD. Hybrid catalysts for direct synthesis of DME were prepared by physically mixing the dry pre-pelletized metallic and acid catalysts in a 8-to-1 ratio (mass based). For the sake of comparison, γ-alumina (PURALOX 5/200 from Sasol Germany) was also used in a few experiments as the dehydration function of the hybrid catalyst in an Al/CZ ratio of 2. All catalysts were used as powders in a particle size range of 80-125 μm. The methanol dehydration experiments were performed over zeolite diluted with α-alumina, which was prepared by treating PURALOX 5/200 at 1150℃ overnight. The structural change from γ to α-Al_2O_3 was confirmed by XRD.

Fresh and used catalysts (except for CZ-C1 and -C2) were characterized by various techniques. The BET surface area was estimated from the nitrogen desorption isotherm at 77K, measured using a Micromeritics TriStar 3000. Samples were outgassed overnight under 0.05 mbar pressure at 200℃ prior to the measurements. Powder X-ray diffraction (XRD) analyses were done using a Bruker D8 Focus powder diffractometer equipped with a Lynx-

Eye™detector, using Cu Kα radiation. The samples were analyzed between the 2θ angles of 15° and 80°, and the diffraction data were analyzed using the Bruker DIFFRACplus EVA software. Present phases were identified by a search/match procedure using the 2009 edition of the ICDD PDF4+ database. In addition, the Bruker DIFFRACplus TOPAS software was used for quantitative phase analyses (Cu crystallites size by applying the Scherrer equation on Cu(111) peaks). X-ray photoelectron spectroscopy (XPS) was applied to detect possible accumulation of carbon, Fe or Ni on the catalyst surface after experiments and identify the oxidation state of Cu and Zn. An Axis UltraDLD XP spectrometer from Kratos Analytical was used and selected catalyst samples were analyzed using both monochromatic Al Kα and achromatic Mg Kα X-ray sources. Samples were outgassed under $10^{-8} - 3 \times 10^{-9}$ Torr pressure in the analysis chamber. Elemental analysis of the catalysts was done using a Thermo Scientific Element 2 high resolution ICP-MS. Powdered ZSM-5 and CZ samples were mixed with, respectively, a concentrated HNO_3-HF mixture and a 50% v/v HNO_3 solution, digested in an ultrasonic bath at 80℃ and then diluted prior to analysis. The acidity of the zeolite samples were measured by NH_3-TPD method in a NETZSCH STA 449C thermo-microbalance coupled with a QMS 403C mass spectrometer. The samples were pre-treated in situ at 600℃ for 1 h, prior to adsorption taking place at 100℃ under a gas flow composed of 1% NH_3 in Ar for 30 min. Samples were then purged with Ar for 1.5 h at 100℃ before thermal desorption spectra being recorded by increasing the temperature from 100 to 800℃. Thermal and oxidative treatment of deactivated zeolite samples were also performed in the same instrument. TPD spectra were obtained between

200 and 600℃ under Ar flow, after a 40 min in situ pre-treatment at 200℃. Subsequently, the samples were exposed to oxygen by substituting argon flow with air at 600℃.

2.2. Reactor and experimental setup

The methanol dehydration experiments were conducted in an isothermal stainless steel tubular fixed-bed reactor (ID=9 mm). The reactor was clamped in between two half-cylindrical aluminum blocks to ensure a uniform heat transfer, and placed in a Kantal oven equipped with a Eurotherm temperature controller. Temperature was monitored in the catalyst bed (∼1 cm) by moving the thermocouple along a thermowell installed along the axis of the reactor. To keep the reaction temperature fully under control, the highly exothermic methanol and direct DME syntheses experiments were conducted in a stainless steel fixed-bed microstructured reactor-heat exchanger, fabricated in Karlsruhe Institute of Technology, Germany. The reactor consists of a 6 cm-long reaction slit with rectangular cross section of 8.8 mm×1.5 mm, sandwiched between cross flow channels for circulation of heat transfer oil. The reaction temperature was monitored by inserting several thermocouples into the dedicated holes on top of the reactor housing along its center line, which provides proximity (∼2 mm) to the catalyst bed. The pressure drop of the catalyst bed was measured before and after each experiment using a pressure transducer to confirm insignificant changes in catalyst packing. The micro-structured reactor has been thoroughly studied earlier in our group for methanol [48–50], direct DME [51–53] and Fischer-Tropsch [54] syntheses, and has been established as practically isothermal, isobaric and free from mass transfer limitations under conditions similar to the ones applied in the

present study.

Premixed synthesis and carrier gases were of 5.0 quality (99.999% purity) or higher. Compositions of the gases used are summarized in Table 1. The gases were fed through digital mass flow controllers (Bronkhorst), and pressure was controlled using a digital back pressure controller (Bronkhorst). Introduction of methanol or water was done by evaporating the pressurized liquid into the feed gas stream using a Controlled Evaporator Mixer (Bronkhorst). To investigate the effect of impurities on deactivation, pulses of xylene was injected into the feed, by first evaporating ∼1 g xylene in a small sample cylinder and then redirecting the feed flow to pass through the container. Feed and product tubing was heated to ∼180℃ to eliminate temperature gradient at the catalyst bed inlet and prevent condensation of water, methanol and trace concentrations of other possible liquid products. The products were analyzed online using an Agilent 7890 gas chromatograph, equipped with a thermal conductivity and flame ionization detectors. Nitrogen and CH_4 were used as internal standards to perform the calculations. The carbon mass balance over the system closes within 5% or smaller (often below 3%) error margin at all times. The error is caused partly by not quantifying the hydrocarbon byproducts of methanol dehydration. Blank tests confirmed inactivity of the setup and α-alumina dilutant.

3. Results and discussion

3.1. Deactivation of methanol synthesis catalyst

Fig. 2 presents an example of the activity loss during methanol synthesis, both as a drop in normalized methanol formation rates (left axis) and as a

Table 1: Compositions (mol%) of the applied synthesis and carrier gases.

	H_2	CO	CO_2	CH_4	N_2
Syngas-1	42	42	5	6	5
Syngas-2	56	28	5	6	5
CGas-1	0	0	0	5	95
CGas-2	42	0	0	3.4	64.6
CGas-3	0	42	0	3.4	64.6

reduction in absolute CO conversion values (right axis). Comparable levels of deactivation were observed for all methanol synthesis catalysts under similar operating conditions. Fig. 2 also clearly shows the importance of monitoring catalyst deactivation at low conversion levels, as the data measured at a lower space velocity (resulting in higher conversion) suggests a considerably lower deactivation due to the effect of equilibrium on the syngas conversion.

Pure premixed synthesis gas was used for the experiments (impurity level below 10 ppm) and common poisons such as S and Cl were not present in any of the raw materials used. Iron and nickel carbonyls, however, could in theory form inside the reactor, tubing or gas cylinders (if the internal surface is not coated with aluminum) from steel in contact with syngas. For this reason, a carbonyl trap containing PbO was installed upstream of the reactor. According to the ICP-MS analysis, fresh CZ-H catalyst contains 21 and 2 ppmw of Fe and Ni, respectively. The XPS analyses show negligible amounts of iron and nickel (less than 0.4 mol% total) on the surface of different fresh and used CZ-H catalyst samples, without any obvious trend of concentration change after the reaction experiments. Moreover, XPS confirms no accumulation of

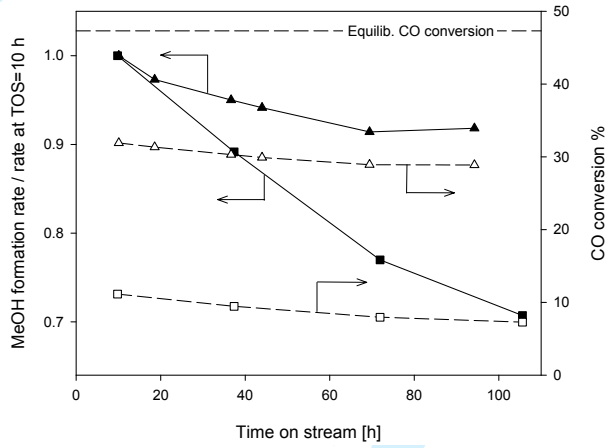

Figure 2: Deactivation of CZ-C2 catalyst during methanol synthesis from Syngas-2, as measured at 250℃, 50 bar and either space velocity of 250 (▲/△) or 800 $Ncm^3/min/g_{cat.}$ (■/□). Solid lines show normalized methanol formation rates on the left axis and dash lines show CO conversions on the right axis. Equilibrium CO conversion is estimated from the Gibbs free energy of the compounds using Aspen HYSYS V8.0 software.

carbon on the catalyst surface even after more than 200 h on stream time. An increase in the surface concentration of carbon could have been a sign of either Fischer-Tropsch activity and wax formation related to the presence of Fe, or less likely, coke deposition on the catalyst as claimed to be happening by Sierra et al. [20, 55–58]. Changes in the BET surface area of the catalyst do not follow any particular pattern and hence, do not provide any information with regard to the catalyst deactivation. The N_2 adsorption analyses of catalysts before and after catalysis indicated a slight increase in the BET surface area of the CZ-H catalyst from ∼63 to 70-75 $m^2/g_{catal.}$, while showed a slight decrease for CZ-C1 catalysts in a similar range.

Copper sintering is known as the main cause of Cu/ZnO-based catalyst deactivation in the absence of poisons [10–12]. Fig. 3 demonstrates the X-ray diffraction patterns of a fresh, freshly reduced and used samples of the CZ-H catalyst. For the fresh sample, only CuO and ZnO peaks are detectable in the diffractogram. Diffraction pattern of the reduced sample confirms the reduction of crystalline CuO to copper crystallites of an average size of 5.3 nm. After being on stream for more than 100 h, average Cu crystallite size of the catalyst grew to 7.8 nm. This can be an indication of Cu sintering. However, it should be noted that ex situ XRD measurements have limitations with regard to possible oxidation of copper upon exposure of the reduced catalyst to the atmosphere as well as the fact that it does not provide direct information regarding the active surface area of the catalyst [59].

Catalyst deactivates slightly faster under Syngas-1 containing 42% CO, than under Syngas-2 with 28% CO. This is in agreement with the reported experimental results suggesting a correlation between the deactivation and

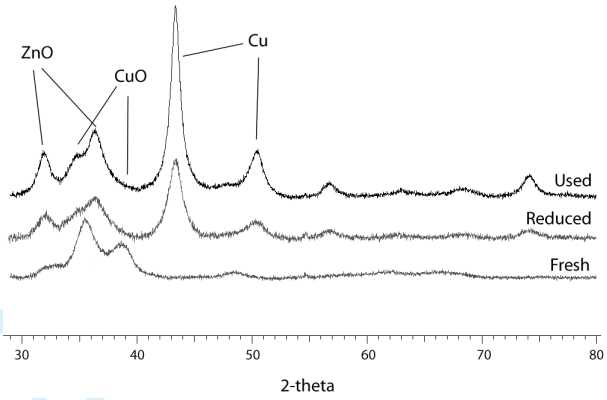

Figure 3: X-ray diffraction patterns of CZ-H in three different states; fresh, reduced and used (operated for 104 h at 210-270℃). Positions of the main peaks correspond to the detected crystalline phases are indicated on the diffractogram.

the CO pressure [35, 60, 61], and the key role of CuCO as the mobile Cu specie in sintering and deactivation of the catalyst, suggested by Rasmussen et al. [13] based on density functional theory (DFT) calculations. The homemade catalyst (CZ-H) is slightly more stable than the commercial catalysts under identical conditions, although much less active. This can be linked to a likely considerably lower Cu content of the CZ-H, and higher ZnO content that acts as spacers between the Cu nanocrystals, suppressing their sintering. According to the ICP-MS analysis the $CuO/ZnO/Al_2O_3$ molar ratio of the CZ-H is 25/65/10, as opposed to ∼60/30/10 mol% expected for the typical commercial methanol synthesis catalysts [62].

Ruling out all other known causes of CZ catalyst deactivation, the growth of Cu crystallite seems to be the sole cause of the observed activity loss. Nevertheless, all CZ catalysts showed rather good stability, considering the harsh operating conditions they were exposed to. This could partly have its

roots in the enhanced heat transfer characteristics of the micro structured reactor used, which provides a practically isothermal profile throughout the catalyst bed [50, 51]

It is worth mentioning that the Cu-Zn is a dynamic system and the copper crystallites shape, and hence the catalyst activity, changes reversibly upon alteration of the reaction medium composition [63]. Transient kinetic data indicated that stabilization of the catalyst surface and its activity after a change in gas composition may take up to several hours [41, 64]. In our experiments, the initial activity is chosen as the activity after 10 h, much longer than what is needed to reach steady-state (overall C balance with less than 5% error), in order to eliminate the effect of syngas introduction (sudden change in the composition) on the activity changes. Nevertheless, such effects may still partly explain a rather larger drop in the methanol formation rate at the beginning of some experiments.

3.2. Deactivation of ZSM-5

Fig. 4 demonstrates ZSM-5 deactivation during methanol dehydration to DME at 250℃ under a methanol partial pressure of 1.5 bar (for the sake of comparison, equilibrium conversion of Syngas-1 at 250℃ and 50 bar results in P_{MeOH} ∼7 bar at the methanol reactor outlet). At the conditions applied, the initial methanol conversion was around 75% (as opposed to an equilibrium conversion of 88%) and the selectivity towards DME was above 95%. Formation of trace amounts of various hydrocarbons/oxygenates was detected with the GC's flame ionization detector, although identification and quantification of these byproducts were not performed. The color of severely deactivated H-ZSM-5 samples changed from white to yellowish brown. Such

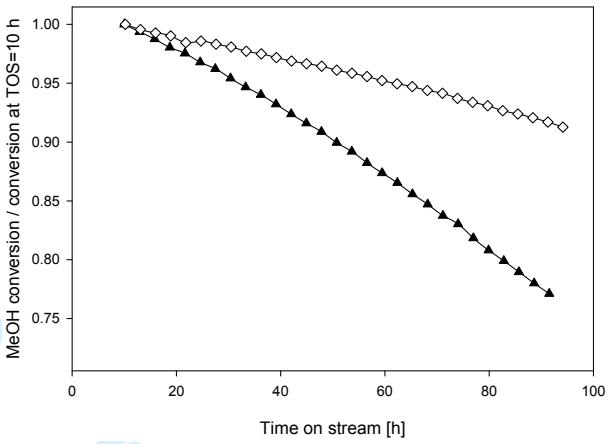

Figure 4: Deactivation of H-ZSM-5 (▲) and NaH-ZSM-5 (◇) during methanol dehydration to DME at 250℃, P_{total}=10 bar, P_{MeOH}=1.5 bar, using CGas-1 as the carrier gas. Space velocities were chosen respectively as 60 h^{-1} and 40 h^{-1} to yield similar initial methanol conversion level.

color change of the H-ZSM-5 was also reported by Schulz et al. [27, 28, 30] during methanol conversion to hydrocarbons at low temperatures (300℃). They linked the yellow color of the deactivated catalyst to formation and accumulation of highly unsaturated organic compounds at low temperatures, as opposed to the black color of the deactivated H-ZSM-5 during methanol conversion at 450℃, which was explained by coke formation on the outer surface of the catalyst [27, 30]. Measurement of the catalyst surface area with N_2 adsorption before and after the experiments shows a drop in the BET surface area, although no close correlation between the activity loss and the changes in surface area could be drawn. For example, the BET surface area of the deactivated H-ZSM-5 at 58% and 10% of its initial activity were respectively 130 and 123 $m^2/g_{catal.}$, as opposed to ∼377 $m^2/g_{catal.}$ for the fresh zeolite.

To obtain further information regarding the nature of deactivating species, used catalyst samples were subjected to heat treatment under inert atmosphere (Ar flow), followed by oxidation at high temperature. An example of the results is presented in Fig. 5. The TPD spectrum was recorded between 200-600℃ in a thermo-microbalance, after pre-treatment at 200℃ to remove species that might be adsorbed on the catalyst after the reaction. The mass reduction of the sample upon heating indicates desorption of species between 300 and 400℃, peaking around 320℃. With the small amount of sample that could be accommodated in the sample holder, the compounds desorbed were too diverse and too low in concentration to be detected with good precision using the mass spectrometer coupled with the microbalance. Following the TPD, argon flow was substituted with air at 600℃. Upon introduction of oxygen, a sudden but small reduction in the sample mass was detected along with evolution of CO_2 and water in the effluent, indicative of oxidation of remaining adsorbed carbonaceous compounds on the catalyst. These results suggest that the main part of the products retained on the catalyst during methanol dehydration to DME at 230-270℃, decompose/desorb at 300-400℃ and only a small part is sufficiently stable to remain on the catalyst even at temperatures as high as 600℃. This latter part likely has coke like characteristics, and if so, should have been formed on the outer surface of the catalyst since the ZSM-5 pore system strongly prohibits formation of multicyclic aromatic compounds inside the channels [30].

The results from the thermogravimetric analyses are consistent with the results of a comparable study conducted by Schultz et al. and their suggested deactivation mechanism [27, 28, 30–32]. They studied H-ZSM-5 cat-

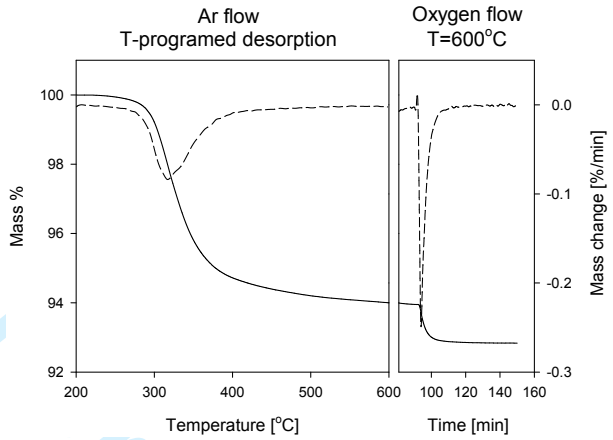

Figure 5: Thermal (left panel) and oxidative (right panel) treatments of H-ZSM-5 deactivated during methanol dehydration at 230-270℃ and SV=7 h^{-1}. Solid and dashed lines shows normalized sample mass and mass changes, respectively.

alysts deactivation during methanol conversion to hydrocarbons (MTH) at low temperatures (270-290℃), using TPD, and reported desorption of retained compounds between 200-400℃ with a maximum occurring at around 310℃ (increasing slightly with the MTH reaction temperature at which the catalysts were deactivated) [28]. A sophisticated sampling technique was used to enable detailed analysis of the effluent gas during TPD. Results confirmed desorption of a wide range of aromatics, olefins and paraffins from the used catalyst upon heating, with trimethyl benzene and xylene as the dominating aromatics and ethene and propene as the main aliphatic hydrocarbons. Furthermore, their direct analyses of the retained compounds after dissolution of the encapsulating zeolite network in HF and extraction of the organic fraction with a solvent indicated that retained hydrocarbons are mainly composed of multi-alkylated benzene molecules. Consequently,

Schultz et al. concluded that, at low temperatures, H-ZSM-5 deactivates due to formation (and accumulation) of bulky mono-ring arenes inside the zeolite pores through irreversible alkylation of benzene rings with light olefins (see Fig. 1). The alkylation reaction becomes reversible at higher temperatures, allowing deactivating bulky aromatics to escape the zeolite after dealkylation to smaller molecules [25–32].

Along with H-ZSM-5 deactivation, Fig. 4 also presents the deactivation behavior of $Na_{12\%}H_{88\%}$-ZSM-5. The ion-exchanged zeolite with acid site density of 1.47 mmol/$g_{catal.}$, shows almost 10% less acidity in comparison with the parent zeolite (1.63 mmol/$g_{catal.}$), as measured by NH_3-TPD. Deactivation of the two catalysts was compared under identical conditions, except for different space velocities that were chosen in a way to yield similar level of initial methanol conversion. The zeolite with lower acidity demonstrates a better stability, but as expected, a lower activity. The initial methanol conversion rate over NaH-ZSM-5 was $\sim$287 μmol/s/$g_{catal.}$ as opposed to $\sim$385 μmol/s/$g_{catal.}$ for H-ZSM-5 under the identical conditions specified under Fig. 4. The activity of ZSM-5 for methanol dehydration to DME is usually determined by its Brønsted acid sites, although the contribution of EFAl-related strong Lewis acid sites cannot be ignored completely [17, 44]. Since methanol dehydration to DME does not require strong Brønsted acid sites (unlike methanol conversion to hydrocarbons), partial deactivation of these sites with e.g. sodium or ammonia, or using a zeolite with lower acidity (higher Si/Al ratio) is known to improve DME selectivity and catalyst stability, though at a cost of reduced activity. [18, 65].

Fig. 6 provides some insights into the effect of temperature on H-ZSM-5

deactivation during methanol dehydration to DME. In comparison to the deactivation rate at 250℃, the catalyst seems to deactivate slower at both higher (290℃) and lower (210℃) temperatures. This observation is in agreement with the results reported by Schulz and Wei [28] with regard to H-ZSM-5 deactivation during methanol conversion to hydrocarbons at 260-290℃. According to their study, the rate of hydrocarbon formation (either volatile or retained on the catalyst), and hence, the rate of catalyst deactivation decreases by lowering the temperature and drops considerably below 270℃. On the other hand, H-ZSM-5 deactivation through pore filling by the retained hydrocarbons decreases as the temperature increases. This is explained as a result of an equilibrium shift towards the reactants in the benzene alkylation reactions, and therefore, dealkylation of the bulky hydrocarbons which are trapped in the zeolite pores to smaller molecules that can diffuse out of the channels. As a result of these two contradicting effects, the maximum deactivation rate was observed at 270-280℃ in the temperature range investigated.

Considering the low rate of hydrocarbon formation at low temperature and short contact time relevant for DME production, it is worth stressing that the presence of hydrocarbon impurities, in the feed or on the catalyst, may also play a role in the zeolite deactivation. The MTH reaction follows a hydrocarbon-pool mechanism, and methanol reacts much faster with hydrocarbons in the pool rather than directly with other methanol molecules [21]. Considerably lower initial conversion rate when highly purified reactant feed and catalysts are used [66] suggests that the direct methanol or DME conversion is of little practical importance even for formation of the "first"

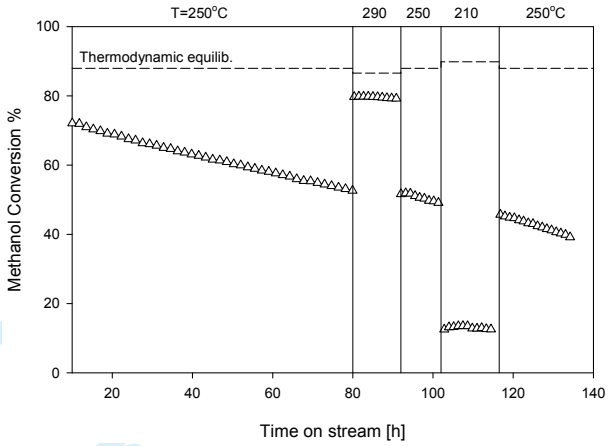

Figure 6: Effect of temperature on deactivation of H-ZSM-5 during methanol dehydration to DME at P_{total}=10 bar, P_{MeOH}=1.5 bar, and SV=60 h^{-1} using CGas-3 as the carrier gas. Equilibrium methanol conversion is estimated from the Gibbs free energy of the compounds using Aspen HYSYS V8.0 software.

C-C bonds, since such reactions, if taking place, proceed at a rate so low that they are eclipsed by the reaction of methanol with trace hydrocarbon impurities from various sources. Therefore, the deactivation behavior of the zeolite catalyst during methanol dehydration at low temperatures may be sensitive to the presence of carbonaceous impurities. Nevertheless, no effect on the deactivation trend of the H-ZSM-5 was observed after several injections of xylene to the reactor feed (pulses of ∼1 g xylene evaporated into the feed stream) during methanol dehydration at 250℃. According to the deactivation mechanism discussed earlier (see Fig. 1), xylene is one of the key intermediates leading to formation of the deactivating species.

For the sake of comparison, the deactivation of γ-alumina was also examined under conditions identical to the ones used for H-ZSM-5 in Fig 4. As expected, the methanol dehydration activity was much lower over γ-Al_2O_3

(methanol conversion rate of ∼106 μmol/s/$g_{catal.}$) in comparison with H-ZSM-5 (∼385 μmol/s/$g_{catal.}$). Alumina experienced a rather dramatic activity loss (20% drop in methanol conversion) in the first 10 h on stream, probably due to the well-known competitive adsorption of product water on the active sites [17–20]. After TOS of 10 h, deactivation was comparable to the H-ZSM-5 deactivation, although under very different methanol conversion levels, 20% as opposed to 75%.

3.3. Deactivation of the hybrid catalyst

In addition to the aforementioned deactivation modes for CZ and H-ZSM-5 catalysts, it is investigated whether conditions created due to combining methanol synthesis and methanol dehydration in a single unit can affect the deactivation of either components of the hybrid catalyst for direct DME synthesis. The hybrid catalysts were prepared by physically mixing the pre-pelletized CZ catalysts with solid acid catalysts as previously mentioned.

3.3.1. Effect of methanol dehydration on CZ deactivation

A possible effect from methanol dehydration on the stability of CZ catalyst may originate from the presence of the solid acid catalyst in proximity of the CZ catalyst or the presence of methanol dehydration products, i.e. DME, water or hydrocarbon by-products in the reaction medium. Such effects were investigated earlier in our group as part of a broader study concerning the effects of methanol dehydration on methanol formation reactions [67]. Fig. 7 presents the deactivation behavior of the CZ-C2 catalyst along with three different hybrid catalysts composed of a mixture of CZ-C2 with either H-ZSM-5, NaH-ZSM-5 or γ-Al_2O_3 as dehydration components. Deactivation

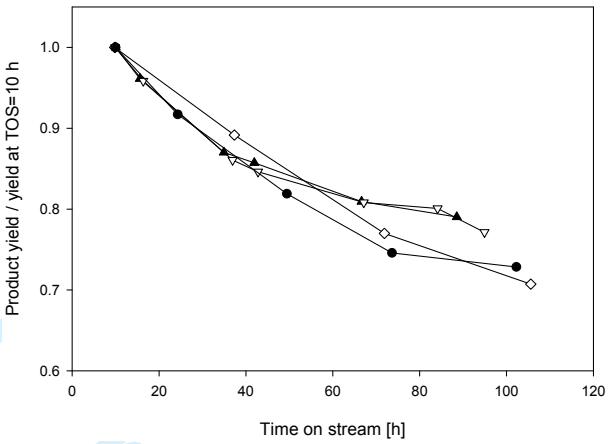

Figure 7: Apparent activity loss of the CZ-C2 catalyst during methanol synthesis (◇) and direct DME synthesis in a hybrid with HZSM-5 (▲), NaHZSM-5 (●), and γ-Al_2O_3 (▽) from Syngas-2. Product yield at T=250℃ and P=50 bar is normalized against the yield at TOS=10 h.

was monitored as a normalized product yield under identical conditions, except for a higher space velocity used for the methanol synthesis experiment that was essential to eliminate the effect of thermodynamic equilibrium on the methanol yield observed. The catalysts were subjected to a sequence of changes in reaction conditions (T=210-270℃, P=10-50 bar) between the data points, however the changes were similar with respect to type, timing and quantity for all the runs. All the experiments were kinetically controlled by methanol formation reactions (hybrid catalysts contain an excess of dehydration function) throughout the studied TOS, and the observed declines in the DME/methanol yield are therefore directly related to the loss of methanol formation activity. Fig. 7 indicates no effect from the methanol dehydration products or either of the solid acid catalysts on CZ catalyst deactivation under the condition applied.

The result is consistent with the experimental results reported by García-Trenco et al. [43–45] confirming no effect from acid catalysts (irrespective of their acidity) on CZ catalyst stability for a hybrid made by mixing pre-pelletized components, as opposed to an enhanced deactivation of the hybrid catalysts prepared by grinding or slurrying (in water) the catalyst components prior to pelletizing. The latter methods are known to create intimate solid-state contact between the two catalysts, which seems essential for detrimental interactions to take place.

3.3.2. Effect of methanol synthesis on ZSM-5 deactivation

The activity of H-ZSM-5 in dehydration of methanol is an order of magnitude higher than the CZ activity for methanol synthesis based on the catalyst mass. For instance, initial methanol formation rate from Syngas-2 over CZ-H at 250℃ and 50 bar was ∼11 μmol/s/$g_{catal.}$, creating a methanol pressure in the range of 1-5 bar (SV=150-700 $Ncm^3/min/g_{catal.}$) in the product stream, while methanol dehydration rate over H-ZSM-5 at the same temperature and methanol partial pressure of 1.5 bar was higher than 385 μmol/s/$g_{catal.}$. Therefore, conducting the direct DME synthesis from syngas under methanol-dehydration controlled regime, i.e. applying a hybrid catalyst with an excess methanol synthesis function, to investigate the possible effect of methanol synthesis on H-ZSM-5 deactivation was not possible due to practical reasons (limitations regarding reactor volume and flow range of the mass flow controllers). Instead, the acid catalyst was used alone and the methanol synthesis conditions were simulated by using syngas (partial pressure around 8.5 bar) as the carrier gas for evaporation and introduction of methanol.

Fig. 8 compares H-ZSM-5 deactivation during methanol dehydration us-

ing carrier gases with different compositions (H_2 and CO contents), under otherwise identical conditions. All gas mixtures contain N_2 and CH_4, which are used as internal standards for GC analyses. The initial methanol conversion level was in the range of 72-77% for all the experiments, and despite the slight differences in the initial activity, the results cannot confirm any effect from the carrier gas composition on activity. The deactivation data shows a higher H-ZSM-5 deactivation rate under carrier gases containing CO and a lower rate for carrier gases containing H_2, suggesting a positive effect from H_2 and a negative effect from CO on H-ZSM-5 stability. A similar conclusion can be drawn from other sets of experiments where changes in the carrier gas composition during the course of one experiment led to alterations in the catalyst deactivation rate. These observations are in agreement with the experimental results reported by Barbosa et al. [40] and Erena et al. [41], where a higher H_2/CO ratio of the synthesis gas was suggested to restrain the formation of deactivating compounds and deactivation of the CZ/ZSM-5 hybrid catalysts. In both studies, deactivation of the hybrid catalysts was linked to deposition of carbonaceous species, which were formed on the acid function of the hybrid (probably through MTH reactions), but deposited on the methanol synthesis catalyst. Erena et al. speculated the reaction of hydrogen with coke precursors as the origin of the reduced deactivation under higher P_{H_2} [41].

During the first few hours of the experiments (TOS<10), different patterns of methanol conversion development with TOS were observed under different gas compositions, conveying an impression of a potentially important effect from H_2/CO ratio of the gas on methanol conversion. However,

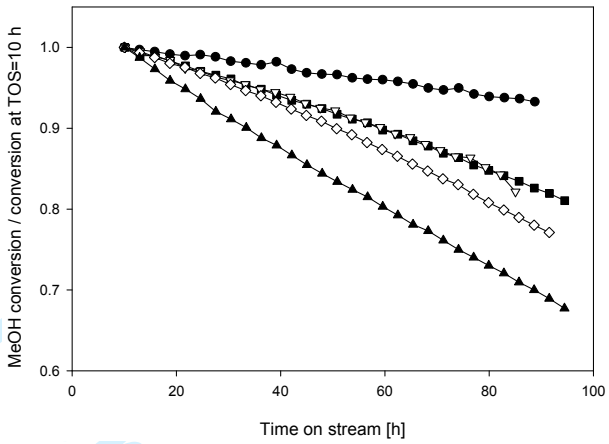

Figure 8: Deactivation of H-ZSM-5 during methanol dehydration to DME using different carrier gases for methanol introduction; Syngas-1 (▽), Syngas-2 (●), CGas-1 (◇), CGas-2 (■) and CGas-3 (▲). T=250℃, P=10 bar, X_{MeOH}=15%, WHSV=60 h^{-1}. Methanol conversion is normalized against the conversion at TOS=10 h.

such observations seems highly influenced by unsteady-state conditions at the beginning, and a reliable investigation of these events was limited by the time resolution of the analyses.

CO_2 is only present in small amounts in two of the gases and its possible effect on H-ZSM-5 deactivation cannot be evaluated based on the experiments performed. Methanol dehydration to DME on Lewis acid sites of γ-alumina or ZSM-5 (electron-deficient Al), is known to require adjacent Lewis base sites (electron-rich oxygen bonded to Al) to proceed [68–71]. Similarly, Lewis base sites play an important role in all the proposed methanol dehydration mechanisms on Brønsted acid sites (acidic proton) [72–82]. In theory, the presence of CO_2 as a weak acid can potentially affect methanol dehydration through possible interaction with the basic sites. Such inhibitory effects have been observed from phenol or acetic acid (stronger acids in comparison with

CO_2) for dehydration of alcohols to ethers on alumina-based catalysts [70]. Xu et al. [17] claimed that the basic sites of γ-alumina are not sufficiently strong to interact with CO_2 and they confirmed no effect directly from CO_2 on methanol dehydration.

The effect of CO_2 on deactivation of H-ZSM-5 should also be considered from another perspective. In the presence of Cu-based methanol synthesis catalyst (which also has high water-gas shift activity), the CO_2-content of the synthesis gas is directly linked to the partial pressure of water in the reaction medium. To simulate the effect of CO_2-rich synthesis gas, deionized water was added to liquid methanol feed in the molar ratio of 20/80. This is in the same range as typical water content of the product stream from methanol synthesis unit (crude methanol), i.e. 10-20 mol% water [18]. Fig. 9 compares H-ZSM-5 deactivation during methanol dehydration to DME, with and without the presence of water in the feed, under otherwise identical conditions. For the run with water-methanol mixture as feed, a higher liquid flow and a higher total pressure was used to create a similar flow rate and partial pressure of methanol as in the run with dry feed. The role of water in inhibition of the deactivation is apparent from the presented data. These results are consistent with the positive effects reported for a high CO_2 or water content of the feed on stability of hybrid catalysts during direct DME synthesis [20, 83].

It is worth stressing that, despite the positive effect of water on H-ZSM-5 stability, water may decrease DME yield, both by reducing catalyst activity through competitive adsorption onto Lewis acid sites (which are not the primary active sites of H-ZSM-5 though), and by enhancing reverse reaction

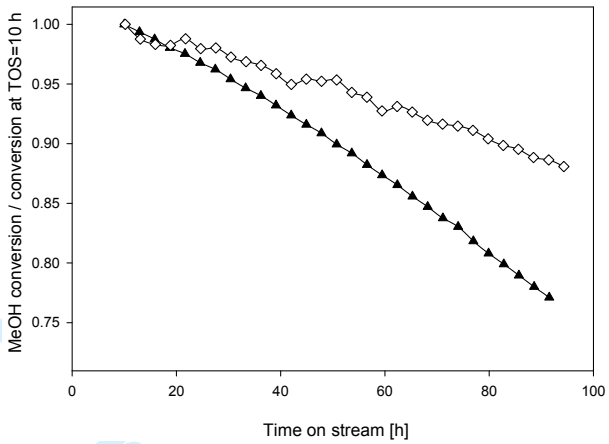

Figure 9: Evolution of methanol conversion to DME over H-ZSM-5 from dry methanol feed (▲) and 19.5 mol% water-in-methanol mixture (◇) with CGas-1 as carrier gas, at 250°C, P_{MeOH}=1.5 bar, SV=60 h^{-1} and P_{total}=10 and 10.4 bar, respectively.

as water is a product of methanol dehydration. With Lewis acid sites as the only active sites, such inhibitory effects are clearly more pronounced for methanol dehydration on γ-Al_2O_3 [17, 20]. For the runs presented in Fig. 9, the initial methanol conversion rate was ∼350 μmol/s/$g_{catal.}$ in the presence of water as opposed to ∼385 μmol/s/$g_{catal.}$ from the dry feed.

3.4. Catalyst regeneration

Deactivation of the zeolite catalysts is much slower during methanol dehydration to DME in comparison to conditions with high contact times and large amount of hydrocarbon formation; for which frequent in situ/continuous catalyst regeneration is required. Nevertheless, in the present study, some efforts were directed towards investigating the possibility of H-ZSM-5 regeneration, deactivated during methanol dehydration to DME. Considering the nature of the deactivating hydrocarbons, one potential means of recovering H-

ZSM-5 activity is in situ thermal treatment of the deactivated catalyst in an inert environment. According to the results of the temperature-programmed desorption analyses presented earlier, deactivating species are expected to decompose and escape the catalyst below 400℃. As the first attempt, a severely deactivated H-ZSM-5 at 27% of its initial activity was subjected to heating from 250 to 450℃ (with the rate of 2℃/min) under N_2 flow, followed by a 3 h dwell at 450℃, before being cooled back to 250℃. The gain in activity was ∼25%, which is nevertheless only around 3% of the initial activity. A similar procedure with a longer period of heat treatment (14 h) was applied for a less deactivated H-ZSM-5 (80% of the initial activity), and the catalyst activity was recovered to 90% of the initial activity. Such a method, even if efficient for H-ZSM-5, is not applicable for direct DME synthesis catalyst due to the severe thermal deactivation of the methanol synthesis component at such high temperature.

Heat treatment in the presence of steam and/or oxygen is a common method for reactivation of the catalysts deactivated by coke [84]. Although coke is not expected to be the main cause of the H-ZSM-5 deactivation during DME production, regeneration of the DME synthesis catalyst through addition of steam or oxygen to the feed has been reported successful by several researchers [20, 58, 83]. Therefore, the usefulness of treatment with steam and O_2 was briefly investigated at temperatures that can be tolerated by the methanol synthesis catalyst. In order to evaluate the effect of water, during the course of methanol dehydration at 250℃ and P_{MeOH} of 1.5 bar, 1.5 bar steam was added to the reactor on the catalyst severely deactivated to 10% of its initial activity. Steam could not recover the H-ZSM-5 activity

at this temperature, but further deactivation was largely reduced as long as the water was fed. The effect of co-feeding water on reducing deactivation rate of H-ZSM-5 was discussed earlier. Despite our observations, Jun et al. [83] reported a recovery of the H-ZSM-5 activity from ∼55% DME yield to almost 80% (initial yield ∼90%) by addition of 65 Torr water to the feed (67 Torr methanol) at 250℃.

The last regeneration method examined was controlled oxidation of carbonaceous compounds of deactivated H-ZSM-5. Such treatment may also be efficient for reactivation of the metallic component of the hybrid catalyst deactivated by Cu sintering, through the oxidation-reduction method proposed for redistribution of sinterd copper [85–89]. Oxidative treatment of H-ZSM-5 was performed using a partially deactivated catalyst at 55% of its initial activity. The reactor was purged with nitrogen and cooled down to 150℃ before air introduction (5%) into the N_2 flow. Subsequently, the reactor was heated up to 250℃ with a heating rate of 1℃/min and finally, at 250℃, the share of air in the flow was increased gradually to 100% over 1.5 h. Despite the expectations, H-ZSM-5 activity dropped to almost 25% of the initial activity after the treatment. In situ reactivation of hybrid catalysts in diluted oxygen, a CZ/γ-Al_2O_3 hybrid catalyst at 325℃ [58] and a CZ/NaH-ZSM-5 hybrid at 260℃ [20], have been reported successful for recovering almost 100% activity even after 10 reaction-regeneration cycles. However, in the both studies, the deactivation was attributed to "coke" formation over the metallic catalyst, while the origin and nature of the deactivating species were not identified clearly. A considerably high selectivity towards paraffins (Fischer-Tropsch activity) reported in both studies (which is expected

from neither typical methanol synthesis nor acid catalysts) could be a sign of catalyst poisoning with e.g. Fe, and hence, a totally different nature of the deactivating hydrocarbons.

4. Conclusion

The objective of the present work was to investigate the deactivation of hybrid catalysts for direct synthesis of dimethyl ether from synthesis gas. For this, deactivation of both functions of the catalyst, i.e. the methanol synthesis function and the methanol dehydration function, were studied individually, first under their typical corresponding conditions, and then under the conditions created by combining both methanol formation and dehydration in a single reactor. In this study, only hybrid catalysts made by physically mixing the pre-pellatized Cu-Zn-based methanol synthesis catalysts and the solid acid catalysts were considered.

Ruling out poisoning, copper sintering was considered as the most likely cause of the methanol synthesis catalysts deactivation. Presence of the solid acid catalysts (zeolite or alumina) showed no additional effect, neither from the catalyst itself nor from the (by)products, on deactivation of the methanol synthesis catalyst. In theory, in situ conversion of synthesized methanol to DME and water could cause a higher partial pressure of water in the reaction medium, assisting copper sintering. However, such an effect cannot be confirmed from our experimental results under the conditions applied.

Accumulation of organic species that are small enough to form inside ZSM-5 cavities, but too large to diffuse out of its channels, is considered as the main cause of ZSM-5 deactivation. Coke formation on the outer surface

of the catalyst may also to a lesser extent contribute to the observed deactivation. Presence of synthesis gas and its composition might have some effects on deactivation of the H-ZSM-5. Presence of H_2 seems to suppress the deactivation while CO appears to enhance it. However, possible effects of impurities on the observed behavior cannot be excluded completely. Addition of water to the feed for a methanol dehydration experiment, simulating direct DME synthesis from CO_2-rich syngas, is shown to decelerate the deactivation, although at a cost of lower DME yield. Similarly, use of CO_2-deficient syngas for direct DME synthesis is expected to reduce the water content of the reaction medium, assisting ZSM-5 deactivation.

Acknowledgment

The authors would like to thank Martin F. Sunding at the Center for Material Science and Nanotechnology, the University of Oslo for his help and insights regarding the XPS analyses. The financial support from the Research Council of Norway (contract No. 208351/E30) is gratefully acknowledged.

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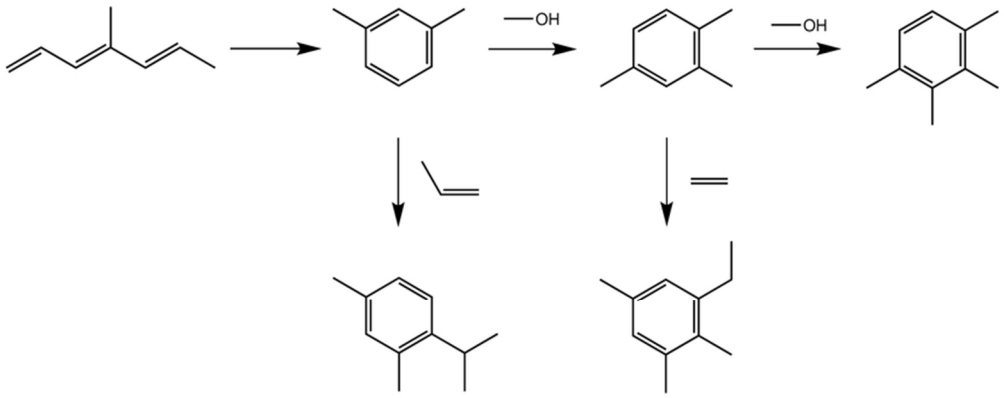

Figure 1

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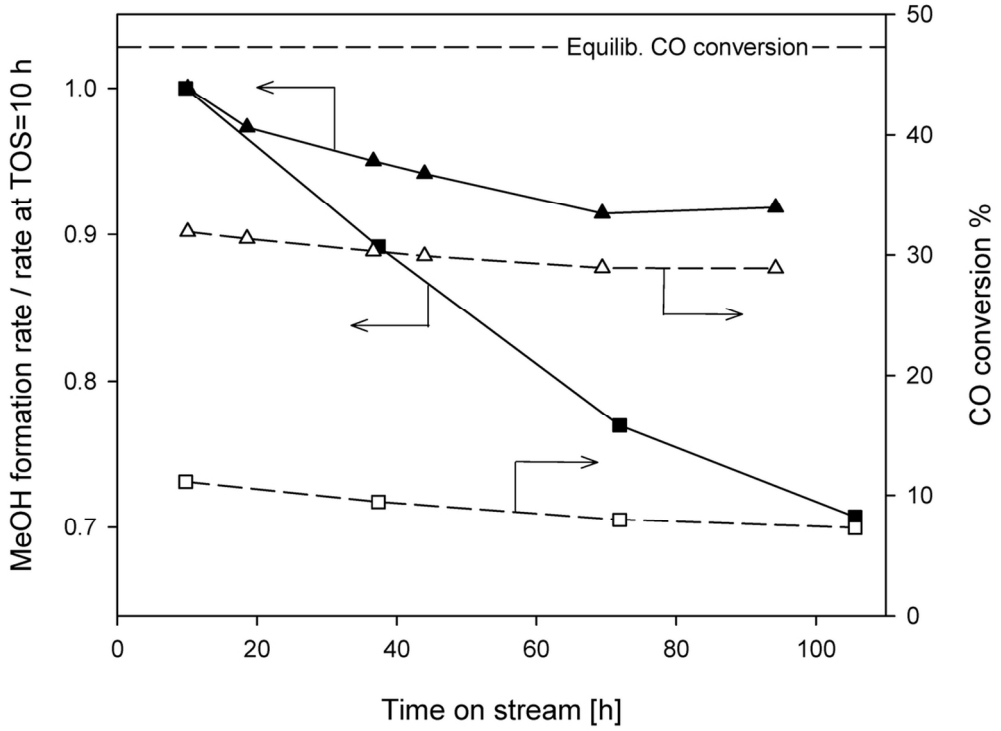

Figure 2

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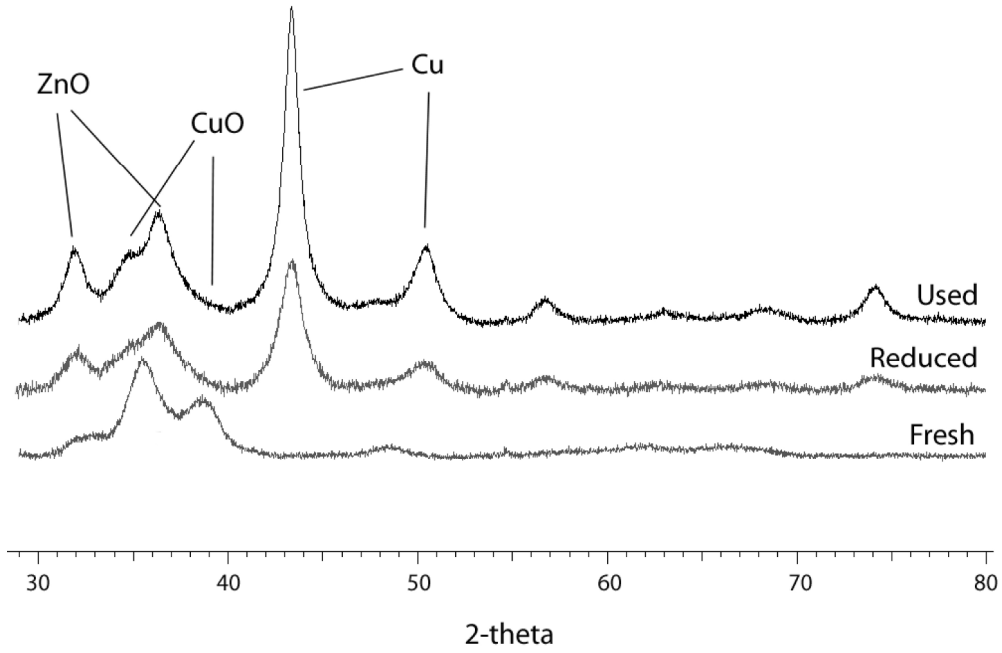

Figure 3

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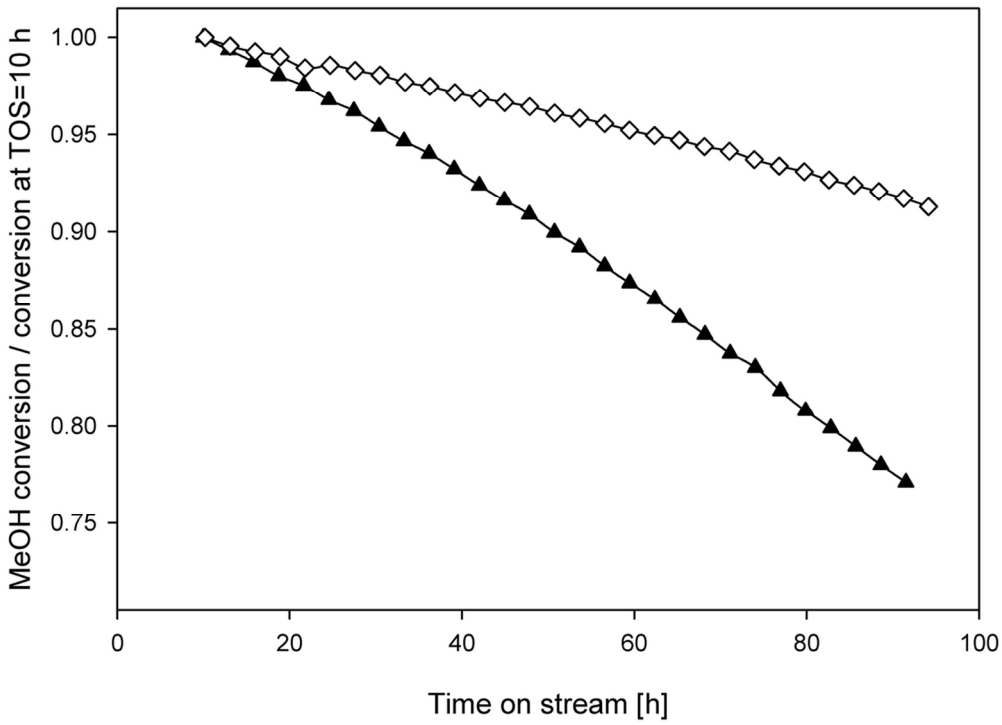

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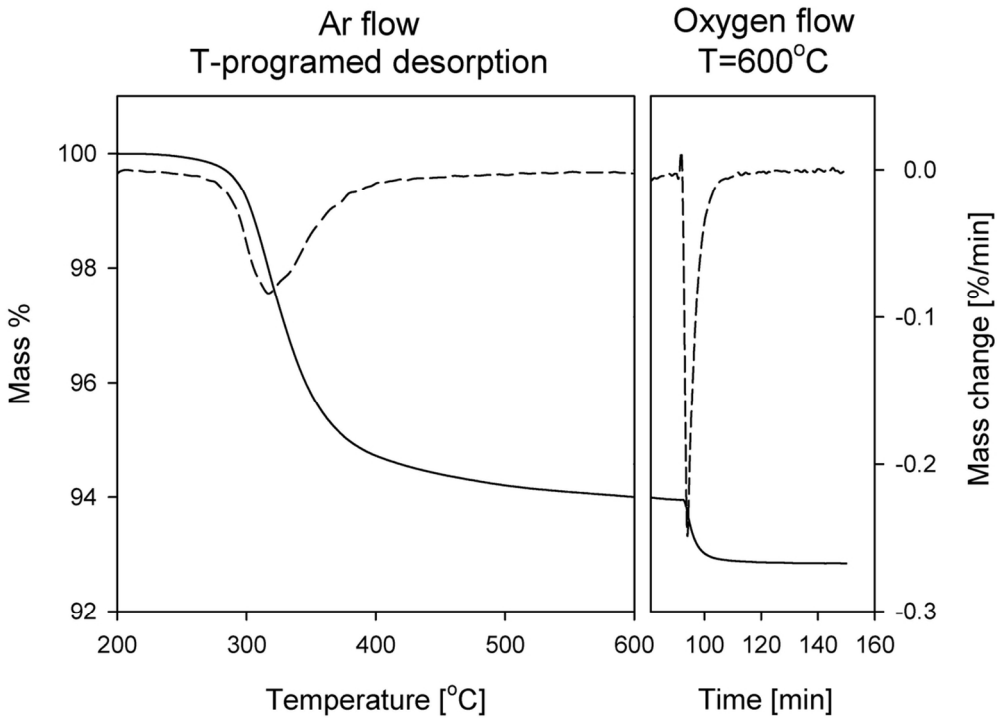

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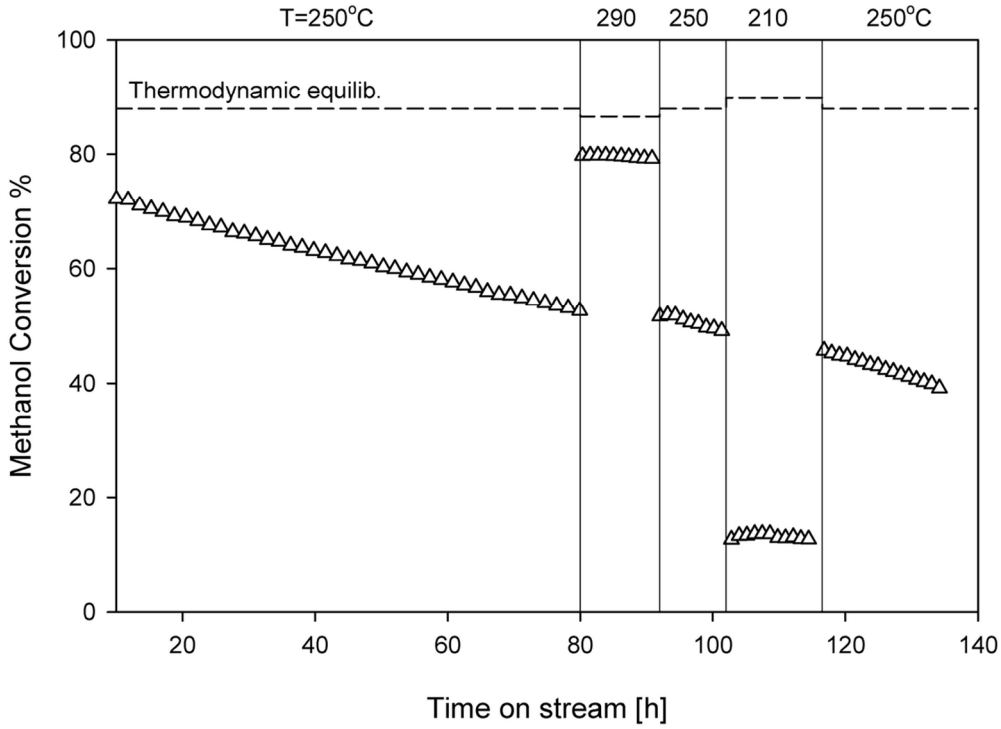

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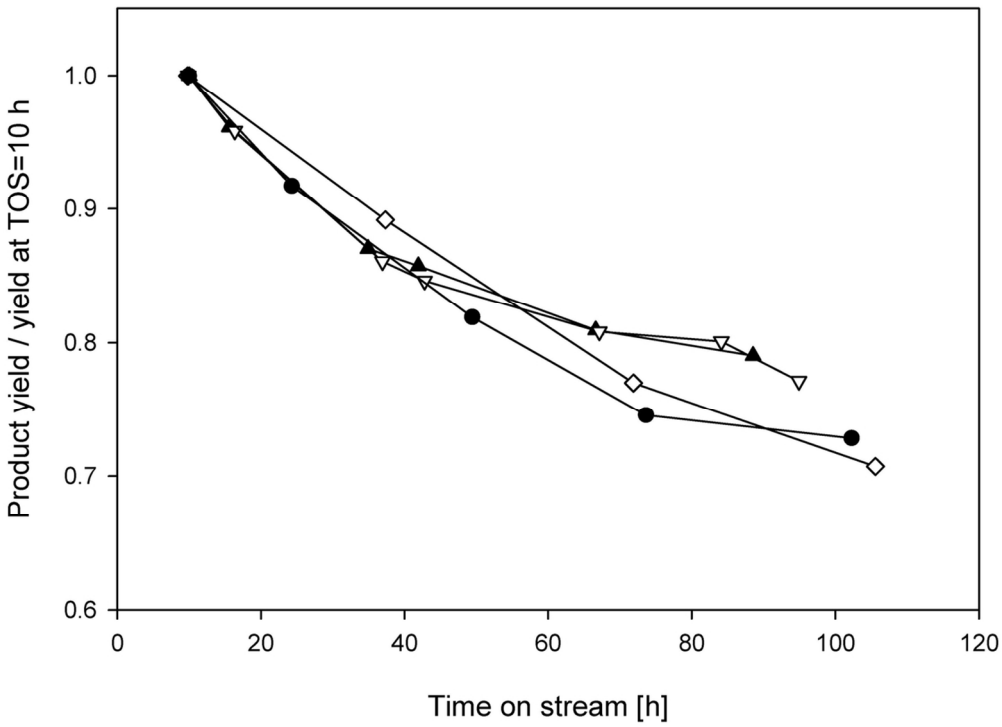

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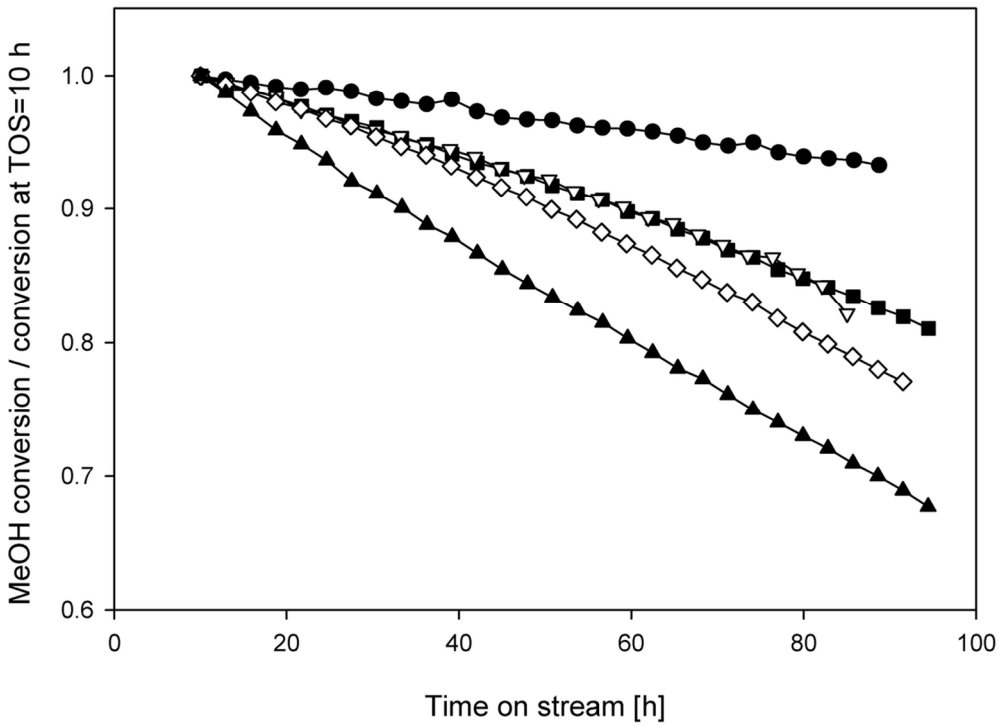

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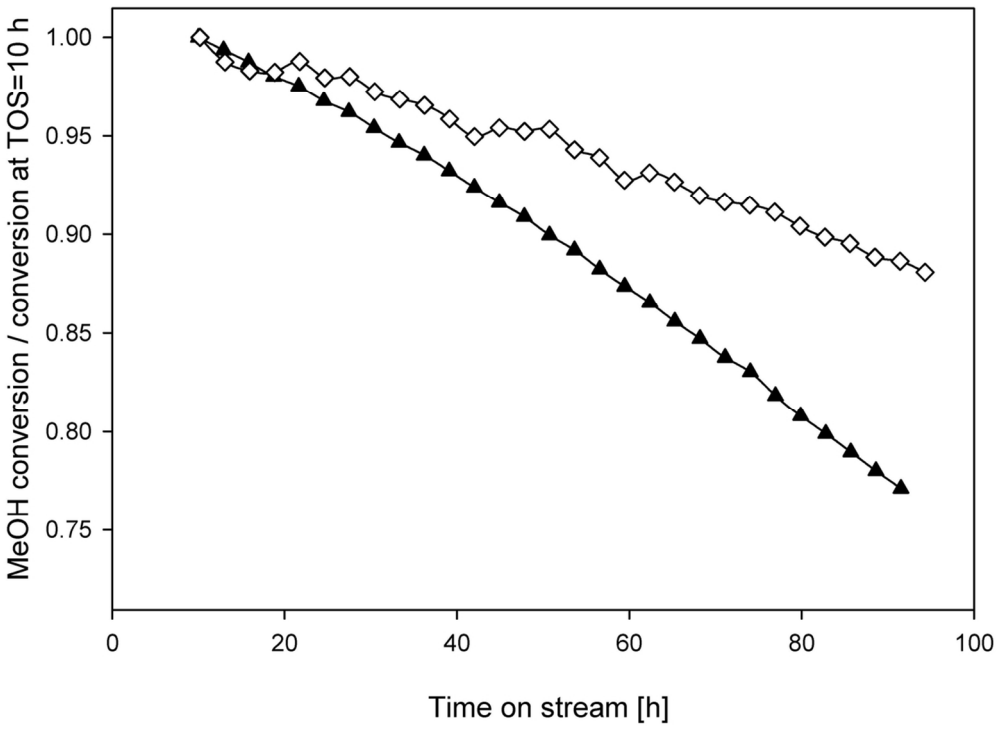

Figure 9

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