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The methyl halide to hydrocarbon reaction over H-SAPO-34

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Abstract

Methyl chloride (MeCl) and methyl bromide (MeBr) were converted to hydrocarbons over a H-SAPO-34 catalyst in a fixed-bed reactor at atmospheric total pressure. The feed rate (WHSV, equivalent to the mass of methanol) was in the range of 0.8–7.7 h^{-1}, and the reaction temperature was varied from 300 to 450 °C. Comparative experiments were performed using methanol (MeOH). An induction period was observed for all reactants. The induction period may be overcome by adding a small amount of propene to the reactor before admission of the methyl halide feed. MeCl and MeBr were converted to the same extent under identical reaction conditions, whereas the methanol conversion was more than one order of magnitude greater than the methyl halide conversion. Product selectivities were similar for all reactants. Partial pressure variations of MeCl (0.1 vs. 1.0 bar pressure) indicated a first-order reaction rate in MeCl at 350–450 °C. Rapid catalyst deactivation was observed for all reactants at and above 350 °C. Repeated reaction–regeneration cycles using 1 bar of MeCl at 450 °C led to a loss of initial activity only, whereas the subsequent activity and product distribution with time on stream were identical for cycles 2–5. No structural changes in the catalyst were observed by X-ray diffraction after the regeneration tests.

Keywords: SAPO-34; Methanol; Chloromethane; Bromomethane; Methyl halide-to-hydrocarbons; Methanol-to-hydrocarbons; Zeolite

1. Introduction

The activation of methane and subsequent conversion to higher hydrocarbons has received considerable research attention. One possible pathway involves conversion of methane to monosubstituted methyl halides and subsequent conversion of methyl halides into hydrocarbons using acidic zeotype catalysts. Methyl halides may be produced through the oxyhydrochlorination (OHC) process [1–3], in which methane is reacted with hydrogen chloride and oxygen to form MeCl and water over a supported copper chloride catalyst [Eq. (1)]. MeCl also may be produced by monohalogenation of methane over supported platinum metal catalysts or supported super acids [Eq. (2)] [4]. In a second step, MeCl, or any methyl halide, may be converted to hydrocarbons and hydrogen halides over acidic microporous catalysts [Eq. (3)]. The hydrogen halide thus produced then may be separated from the hydrocarbon product and recycled back to the halogenation process step [Eq. (1)] [1–3] or may be reoxidized to form molecular halogen [Eq. (4)]:

$$CH_4 + HX + O_2 \rightarrow CH_3X + H_2O, \tag{1}$$

$$CH_4 + X_2 \rightarrow CH_3X + HX, \tag{2}$$

$$nCH_3X \rightarrow C_nH_{2n} + nHX, \tag{3}$$

$$4HX + O_2 \rightarrow 2X_2 + 2H_2O, \tag{4}$$

where X is a halide.

Of the original patents covering the methanol-to-hydrocarbon (MTH) conversion, some also mention the possibility of converting methyl halides to hydrocarbons [5,6]. Previous reports in the regular scientific literature (particularly those by Taylor and coworkers) have focused mainly on the conversion of methyl chloride (MeCl) [7–19]. The possibility of using methyl bromide (MeBr) or methyl iodide (MeI) has been mentioned occasionally [20], but little data are available for comparison. Murray et al. [21,22] have investigated the formation of surface methoxide groups using nuclear magnetic

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resonance spectroscopy and reported the following order of reactivity: MeI > MeBr > MeCl. However, the catalysts that they used were alkali-exchanged, and thus their results may not be relevant for catalytic conversion into light alkenes over acidic materials.

More recently, McFarland and coworkers studied an integrated process for the activation of methane using bromine as the mediator [23–26]. This is a multistep process involving partial oxidation of methane to MeBr, followed by conversion of MeBr to middle distillates over ZSM-5 based catalysts, both acidic- and metal-exchanged.

Su and coworkers have also investigated the reactivity of methyl chloride over microporous catalysts [26–31]. Of particular relevance to the present study is a recent study describing the conversion of methyl chloride to hydrocarbons over H-SAPO-34 and reporting activity/selectivity results and in situ Fourier transform infrared spectroscopy data [31].

In this work, we report the conversion of methyl halides to light olefins over an H-SAPO-34 catalyst, which is a well-known catalyst for the conversion of methanol into hydrocarbons. The H-SAPO-34 catalyst is isostructural to the chabazite framework and consists of fairly large cages (about 7 × 10 Å) connected by eight-ring windows (3.8 Å diameter) [32]. Because of these fairly narrow apertures, only small molecules (e.g., ethene, propene) can diffuse through the openings and out of the catalyst crystals into the gas phase.

Earlier work, conducted primarily with the H-ZSM-5 catalyst, pointed out the similarities in product distribution (and probably also in reaction mechanism) between methanol and methyl halide conversion. Thus, the methyl halide-to-hydrocarbon reaction is closely related to the more widely studied MTH reaction over acidic zeolites [33,34],

$$nCH_3OH \rightarrow C_nH_{2n} + nH_2O. \tag{5}$$

The MTH reaction is generally believed to proceed via a hydrocarbon pool mechanism, in which the hydrocarbon pool consists mainly of polymethylbenzenes [35–44]. Within this mechanistic scheme, the formation of lower olefins (ethene, propene, and butenes) proceeds via continuous methylation and dealkylation (loss of olefins) of aromatic reaction centers. We previously performed theoretical modeling studies that confirmed the feasibility of the hydrocarbon pool mechanism for methyl halides [45].

The main aim of the work reported here was to study the properties of H-SAPO-34 as a catalyst for the methyl halide-to-hydrocarbon reaction. An attempt to use CH_3I as a reactant led to I_2 formation even in the absence of a catalyst; therefore, the study was limited to MeCl and MeBr conversion. Moreover, the conversion and selectivity patterns observed for methyl halides were compared with those observed for methanol. A main idea behind this comparison was to elucidate whether the use of a less active reactant than methanol could change the selectivity of an MTH-like reaction over an identical catalyst.

2. Experimental

The H-SAPO-34 catalyst was prepared by conventional methods [46] and had a $(Al + P)/Si$ ratio of 11, corresponding to 1 acidic site per cage. Scanning electron microscopy (SEM) analysis indicated that the average crystallite size was about 1–2 µm. Before use, the catalyst was calcined in air at 550 °C for 5 h and subsequently pressed and sieved to 0.2–0.5 mm particle size.

Catalytic tests were carried out in a tubular quartz fixed-bed reactor of 9 mm i.d. The temperature in the catalyst bed was measured by a thermocouple inserted in a thermocouple well (3 mm o.d.) centered axially inside the reactor. Before testing, the catalyst (typically 100 mg, diluted with 200 mg of 0.2–0.5 mm quartz particles) was heated to 500 °C in an Ar stream and cooled to the reaction temperature. To overcome a slow induction period (see below), the catalyst was activated by adding 20 Nml of propene to the argon gas stream 10 min before switching from Ar to the feed mixture, normally 10% MeCl or MeBr in He, for a 10 or 100 Nml/min total gas flow. Product formation during propene addition was monitored using an online Pfeiffer Omnistar mass spectrometer, detecting masses of 2 for H_2, 28 and 29 for hydrocarbons, 40 for Ar, 42 for propene, and 44 for propane.

To avoid confusion, in what follows we refer to the feed rate (WHSV, grams of reactant fed per gram catalyst per hour) relative to the molecular mass of methanol, or in methanol equivalents $WHSV_{eq}$, as illustrated by the following example. In an experiment in which 10 NmL of pure gaseous MeX ($X = Cl, Br, OH$) is reacted over 100 mg of catalyst, the following values were obtained: $WHSV_{eq} = WHSV_{MeOH} = 7.7\ h^{-1}$, $WHSV_{MeCl} = 12.2\ h^{-1}$, and $WHSV_{MeBr} = 23.0\ h^{-1}$.

Reactant conversion and product selectivities were measured with a Siemens SiChromat 2–8 gas chromatograph with a JW GasPro column (60 m × 0.32 mm) and a flame ionization detector (FID), along with an HP6890 gas chromatograph with an HP5973 mass-sensitive detector equipped with an identical column. In the case of methanol feed, methanol conversion was determined using a Carlo-Erba 6000 gas chromatograph with a Supelco SPB-5 column (60 m × 0.53 mm × 3 µm) and a FID detector. Typically, the first product analysis was performed after 5 min on stream, and subsequent analyses were performed every 30–40 min thereafter. As indicated by Eq. (3), 1 mol of HX was formed per mole of MeX converted. HX is not listed among the products in the following tables and figures.

Regeneration of deactivated catalysts was performed by heating the catalyst from reaction temperature to 550 °C at a rate of 10 °C/min in an inert gas stream and exposing it to a 10% O_2/He stream at 550 °C for 18 h. After regeneration, the catalyst was cooled to reaction temperature under argon and activated with propene as described above.

Coke amounts in the used catalysts were determined using a thermobalance (Rheometric Scientific STA 1500) and heating to 550 °C at a rate of 10 °C/min in a 10% O_2/N_2 gas stream.

Identification of compounds trapped in the used catalysts was performed by dissolving the catalyst in 15% HF, neutralizing with a NaOH solution, and extracting with CCl_4. The dis-

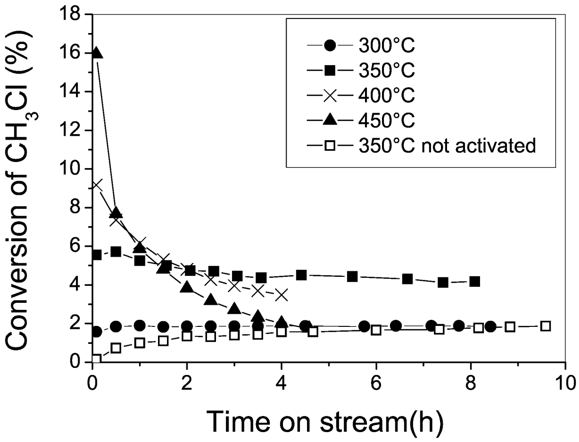

Fig. 1. MeCl conversion versus time on stream at 300–450 °C over SAPO-34, 0.1 bar MeCl, 100 Nml/min, $\text{WHSV}_{\text{eq}} = 7.7\ \text{h}^{-1}$.

solution procedure has been described in detail previously [37]. The organic extract was analyzed by gas chromatography–mass spectrometry (GC-MS) using an HP6890/HP5973 instrument with an HP-5MS column (60 m × 250 µm × 0.25 µm).

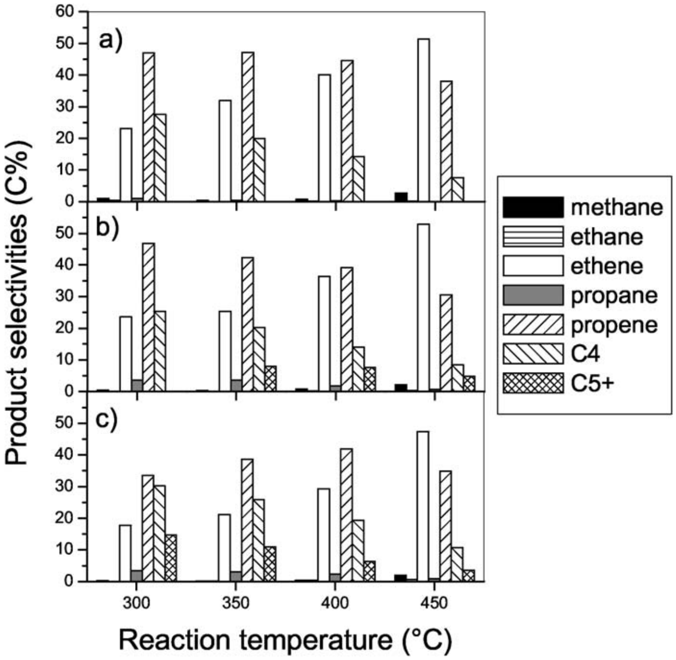

Fig. 2. Product selectivity after 1 h on stream at 300–450 °C over activated SAPO-34. (a) 0.1 bar MeCl, 100 Nml/min, $\text{WHSV}_{\text{eq}} = 7.7\ \text{h}^{-1}$; (b) 0.1 bar MeCl, 10 Nml/min, $\text{WHSV}_{\text{eq}} = 0.8\ \text{h}^{-1}$; (c) 1 bar MeCl, 10 Nml/min, $\text{WHSV}_{\text{eq}} = 7.7\ \text{h}^{-1}$.

3. Results and discussion

3.1. Methyl chloride conversion

Blind tests using 43% MeCl in He (15 Nml/min total flow rate) were performed at 400–500 °C in an empty reactor. No product formation was detected at 400 °C or 450 °C, and even at 500 °C, the conversion was <2%. In addition, the effects of gas-phase reactions at appreciable catalytic conversion were investigated by reducing the hot dead volume (∼2.5 mL) immediately below the catalyst mass in the fixed-bed reactor by filling with inert quartz particles. When 10 NmL/min of neat MeCl ($\text{WHSV}_{\text{eq}} = 7.7\ \text{h}^{-1}$) was converted over the SAPO-34 catalyst at 450 °C, no significant difference in conversion or selectivities could be seen as a function of the dead volume below the catalyst bed. Moreover, the amounts of 2-chloropropane (the most prominent chlorinated compound) formed were identical in the two cases (see below for a more thorough description of the formation of chlorinated products). In summary, compared to the conversions obtained during catalytic tests (see below), the gas-phase conversion of methyl chloride can be considered negligible in all experiments in this study.

MeCl conversion curves versus time on stream at 300–450 °C, reactant partial pressure of 0.1 bar, and total flow rate 100 Nml/min ($\text{WHSV}_{\text{eq}} = 7.7\ \text{h}^{-1}$) are shown in Fig. 1. With an increase in temperature, the initial conversion over the activated catalyst increased from 1.6 to 16% over a 150 °C range. Clearly, a more rapid activity loss with time on stream occurred at elevated reaction temperatures. The initial (1 h on stream) product selectivity distribution at each temperature is shown in Fig. 2a. The olefinic products, especially C_2–C_4, dominated, and the combined selectivity to saturated products was <5 C%. The initial selectivity was shifted toward lighter products with increasing temperatures. These observations are in accordance with those typically observed when MeOH is reacted over H-SAPO-34 [33] and with the results for MeCl conversion over H-SAPO-34 recently presented by Wei et al. [31].

In one test, MeCl was reacted over a non-preactivated catalyst at 350 °C. The initial conversion in this test was very low. After 1 h on stream, the conversion was more than five times greater for the activated catalyst than for the nonactivated sample. However, there was a slow increase in activity for the nonactivated catalyst throughout the 10-h test. The catalyst first activated by propene at 350 °C exhibited a normal deactivation behavior, with the conversion decreasing slightly during the test, although the first analysis point tended to deviate slightly from the trends evident from the following data points. This deviation is likely the manifestation of a minor chemical rearrangement of the hydrocarbons formed from propene in the catalyst pores into the optimum composition for the conversion of methyl halides, that is, methylbenzenes [35–44]. Interestingly, the same effect of propene on the induction period has previously been reported for ethanol conversion over H-SAPO-34 [46]. On-line mass spectroscopy analysis of the reactor effluent during the activation period detected appreciable evolution of hydrogen (m/e 2) and propane (m/e 44) in the effluent during propene addition, indicating the formation of hydrogen-poor species, such as aromatics (see Section 3.5) within the catalyst voids. However, before the introduction of MeX feed (10 min after propene addition), no hydrocarbons (m/z 28, 29, 42) were detected in the effluent.

MeCl conversion curves versus time on stream at 300–450 °C, a reactant partial pressure of 0.1 bar, and a total flow rate of 10 Nml/min ($\text{WHSV}_{\text{eq}} = 0.8\ \text{h}^{-1}$) are shown in Fig. 3, and the product distribution after 1 h on stream is shown in Fig. 2b. The global reactivity pattern is similar to that observed

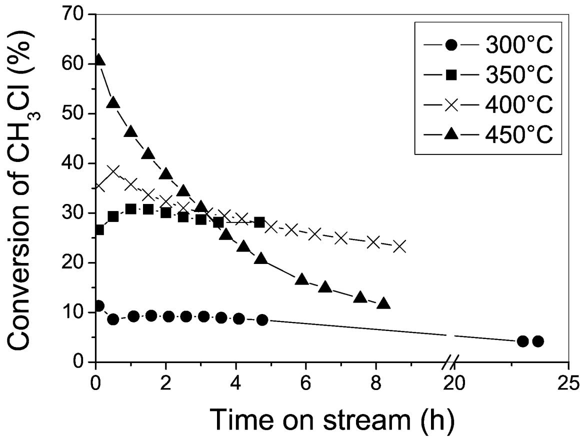

Fig. 3. MeCl conversion versus time on stream at 300–450 °C over SAPO-34, 0.1 bar MeCl, 10 Nml/min, $\mathrm{WHSV_{eq}} = 0.8\ \mathrm{h}^{-1}$. Note the scale break at 10 h.

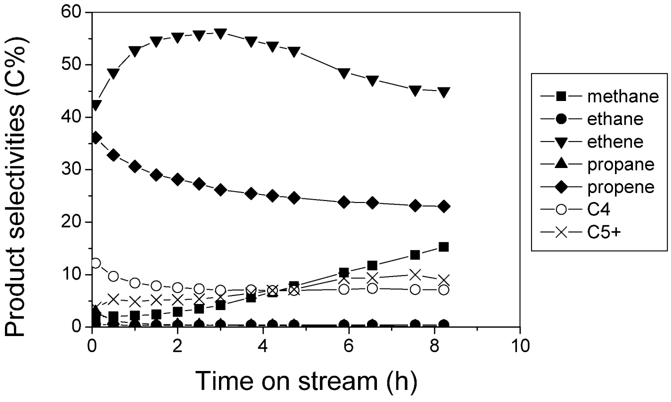

Fig. 4. Product selectivities versus time on stream at 450 °C over SAPO-34, 0.1 bar MeCl, 10 Nml/min, $\mathrm{WHSV_{eq}} = 0.8\ \mathrm{h}^{-1}$.

at higher feed rates; an increase in reaction temperature led to higher conversion (from 11 to 61%), a shift in selectivity toward the lighter products, and more rapid deactivation. Product selectivities versus time on stream at 450 °C are shown in Fig. 4. When the activity decreased with time on stream, the product selectivity shifted toward the lighter products. The same trend can be observed at all temperatures, and similar curves were observed in all MeCl conversion tests carried out here. It should be noted that although the methane selectivity increased steeply with time on stream, the actual yield of methane decreased.

Comparing the activity curves in Figs. 1 and 3 demonstrates that a 10-fold decrease in feed rate led to only a 4- to 6-fold increase in initial MeCl conversion. This deviation from a simple 1:1 proportionality is too large to be explained by the reduction in the effective reactant concentration at low feed rates, at least at the lowest reaction temperatures. We elaborate on this point in Section 3.4. Further, it can be seen from Fig. 2 that the selectivities observed at 1 h on stream are very similar for each temperature, regardless of feed rate, although there is a slight increase in selectivity to saturated products at the lower feed rate.

At 450 °C, the same conversion (16%) was obtained both initially (high feed rate; Fig. 1) and after deactivation (low feed rate; Fig. 3). Hence, it is possible to compare the product selectivities at identical conversion levels but very different deactivation levels. This comparison shows that the ethene/propene ratio is 2.0 for the deactivated sample but only 0.96 for the fresh sample. This result is in line with the findings of Chen et al. in a study of methanol conversion over H-SAPO-34. Chen et al. suggested that transition state selectivity is responsible for the increasing ethene/propene ratio observed for more severely coked catalysts, thus implying that the transition state leading to loss of ethene from the hydrocarbon pool is sterically less demanding than the one leading to propene [47,48]. Another, similar conclusion was reached by Haw and coworkers, who suggested that a reduction of the space within the zeolite cages, which might be caused by coking, will lead to a hydrocarbon pool consisting of methylbenzenes with fewer methyl groups than would be the case if the entire space were available to reactive intermediates, and, further, that the lower methylbenzene homologues tend to yield ethene rather than propene [49,50]. Finally, the enhanced selectivity toward lighter products for more deactivated samples may simply be a manifestation of longer effective diffusion pathways for the products as cage openings become blocked, thus favoring the release of smaller molecules to the gas phase [51]. Various combinations of these effects are certainly possible.

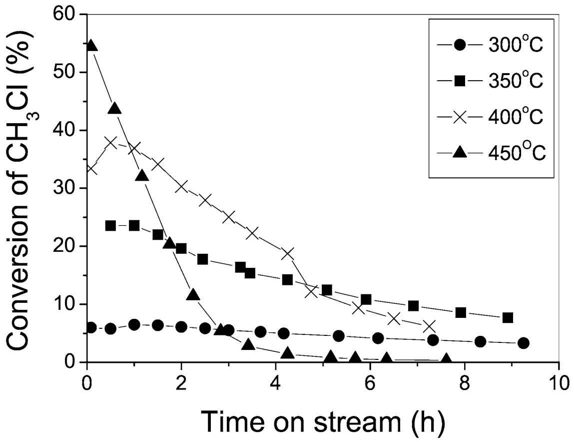

Fig. 5. MeCl conversion versus time on stream at 300–450 °C over SAPO-34, 1.0 bar MeCl, 10 Nml/min, $\mathrm{WHSV_{eq}} = 7.7\ \mathrm{h}^{-1}$.

The conversion versus time on stream curves at each temperature show considerably more rapid deactivation at higher feed rates. However, a more meaningful comparison can be obtained by integrating the curves between 0 and 80% loss of initial activity. At 450 °C, this analysis indicates that 5.4 mmol of MeCl was converted at this deactivation level at the lower feed rate, whereas 3.7 mmol of MeCl was converted at the same deactivation level at the higher feed rate.

Fig. 5 shows MeCl conversion curves versus time on stream at 300–450 °C, a reactant partial pressure of 1.0 bar, and a total flow rate of 10 Nml/min ($\mathrm{WHSV_{eq}} = 7.7\ \mathrm{h}^{-1}$). Comparing the results presented in Figs. 3 and 5, corresponding to a constant total gas flow through the reactor but different reactant partial pressures, shows that the initial conversion is similar, indicating that the reaction is close to first order in MeCl partial pressure at 350 °C and above, but a little lower at 300 °C. Additional data collected at 0.05, 0.10, 0.20, and 0.35 bar of

MeCl at 350 °C (not shown) confirm this first-order dependency. Comparing initial product selectivities (1 h on stream; Fig. 2) indicates a slight shift toward the heavier products at the higher MeCl partial pressure, especially at 400–450 °C. In all cases, the selectivity toward saturated products was $<5\%$.

The apparent catalyst deactivation was more rapid at high MeCl pressure: At a reaction temperature of 450 °C, half of the activity was lost after 90 min on stream at 1 bar, whereas the same activity loss occurred during 200 min on stream at 0.1 bar of partial pressure (Figs. 3 and 5). However, the amount of MeCl converted up to 80% activity loss at 450 °C was 17.1 mmol MeCl at the higher partial pressure, compared with 5.4 mmol at the lower partial pressure, when following the calculation procedure outlined above.

Plotting the (ln rate) versus $(1/T)$ for the MeCl conversion series shown in Fig. 1 gave a slope corresponding to an apparent activation energy of 39 kJ/mol in the temperature range 350–450 °C. Very similar results were obtained for the series obtained at higher MeCl conversions (Figs. 3 and 5). Clearly, this value is too low to constitute a realistic estimate of the intrinsic activation energy for the conversion of MeCl to hydrocarbons. Measurements conducted for the very analogous MeOH to hydrocarbons reaction indicate an intrinsic barrier close to 135 kJ/mol in that case [52]. The first-order behavior described above for MeCl conversion indicates that the surface coverage of MeCl was low during these reaction conditions. Hence, the heat of adsorption will contribute to the apparent activation energy according to the following equation [53]:

$$E_{\text{activation}}(\text{apparent}) = E_{\text{activation}}(\text{intrinsic}) + \Delta H_{\text{adsorption}}(\text{reactant}). \tag{6}$$

Even so, an apparent activation barrier of 39 kJ/mol does appear rather low, implying a significant heat of adsorption for the reactant, in contrast to theoretical calculations and further considerations (see Section 3.6) implying a rather low heat of adsorption for MeCl.

Reactant diffusion limitations must also be considered. Indeed, it does seem clear that diffusion is important, at least for the conversion of MeOH over SAPO-34 and thus most likely for the conversion of methyl halides as well. Chen et al. have proposed that the entry of methanol into SAPO-34 crystallites is limited by diffusion for crystallites larger than 0.25 µm [47], and the sample used in this study comprises 1–2 µm crystallites. Intraparticle reactant diffusion limitations will lead to too-low activation energies, and in such cases the measured activation barrier will be half the value measured in the absence of diffusion limitations. Such a scenario will in many cases also affect the reaction order, except for first-order reactions, for which the original pressure dependency of the reaction rate will be retained [53]. However, the picture is even more complicated for the SAPO-34 catalyst, because the main products, ethene and propene, have kinetic diameters comparable with or slightly larger than those of the reactant [$d_k(\text{MeOH}) = 0.38$ nm, $d_k(\text{MeCl}) = 0.41$ nm, $d_k(\text{MeBr}) = 0.42$ nm, $d_k(\text{ethene}) = 0.39$ nm, $d_k(\text{propene}) = 0.45$ nm] [54–56]. This means that product diffusion might be as important as reactant diffusion, as has been suggested by Barger [51]. The effect of diffusion on the measured barrier outlined above does not account for product diffusion; a more sophisticated kinetic model is needed.

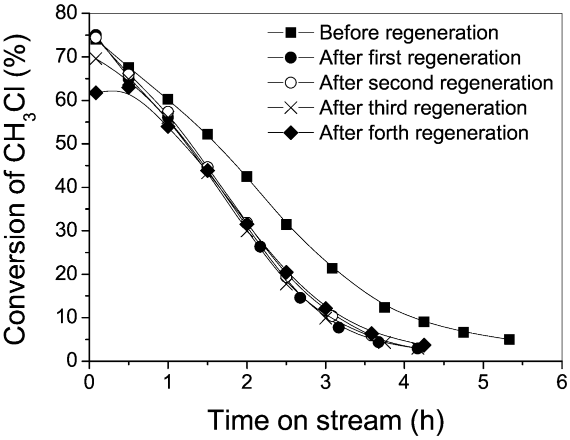

Fig. 6. MeCl conversion versus time on stream at 450 °C over SAPO-34, 1.0 bar CH_3Cl, 10 Nml/min, 200 mg catalyst, $\text{WHSV}_{\text{eq}} = 3.9\ \text{h}^{-1}$. Regeneration in 10% O_2/Ar, 550 °C, 18 h followed by activation with propene at 450 °C.

Finally, the catalyst state at the onset of the MeCl feed must be considered. Analyses of the hydrocarbon pool after catalyst activation show that its composition was significantly altered from 350 to 450 °C (see below). We elaborate on this point in Section 3.5.

Given the complexity of the reaction system with respect to both diffusion and the intrinsic complexity of the hydrocarbon pool mechanism, a clear correlation between apparent activation energies and reaction conditions appears to be beyond the scope of the present study. However, it seems clear that the conversion versus temperature curves are governed by parameters other than reaction kinetics.

Catalyst stability and regenerability were tested by reacting 10 Nml/min 1.0 bar MeCl over 200 mg of catalyst ($\text{WHSV}_{\text{eq}} = 3.9\ \text{h}^{-1}$) at 450 °C until near-complete activity loss occurred, followed by several regeneration/reaction cycles. MeCl conversion curves versus time on stream are shown in Fig. 6. The activity was high (80%) initially and decreased steadily to 5% during a 5-h test. The first regeneration and activation of the catalyst led to full regeneration of the initial activity, but a slightly more rapid deactivation. Subsequent regeneration–reactivation test cycles gave an almost perfect fit to the results from the first regeneration cycle. However, there was a decrease in the initial conversion for the fourth and fifth runs; the measured initial conversions were 74, 75, 74, 69, and 61%, chronologically. Product selectivities after 1 h on stream for each test cycle are shown in Fig. 7. The selectivities were virtually unaltered between the cycles. X-ray diffraction measurements of the fresh and used catalyst (after five reaction cycles) showed no difference between the two samples. Hence, our data show that the SAPO-34 catalyst framework was structurally stable in the presence of the hydrogen halides formed during the conversion of halomethanes to hydrocarbons. Wei el al. [31] reached a similar conclusion in an in situ Fourier transform infrared spectroscopy study of MeCl conversion over SAPO-34. Dissociation of framework Al–O–P bonds to form new P–OH hydroxyl

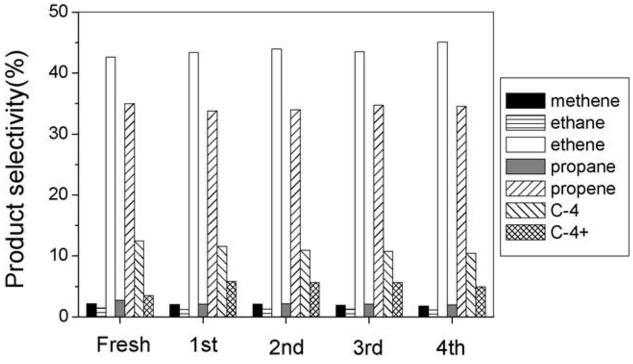

Fig. 7. Product selectivities after 1 h on stream before and after several regeneration cycles; test conditions as in Fig. 6.

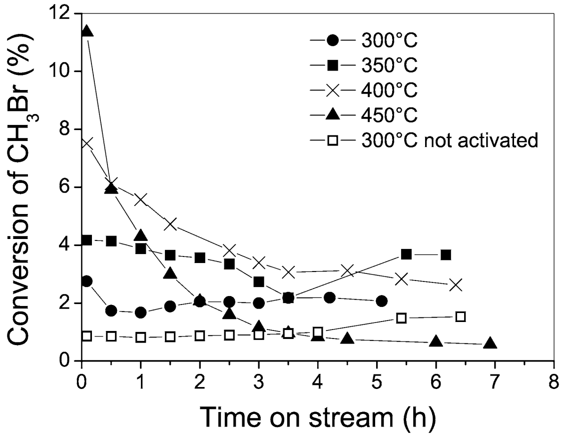

Fig. 8. MeBr conversion versus time on stream at 300–450 °C over SAPO-34, 0.1 bar MeBr, 100 Nml/min, $\text{WHSV}_{\text{eq}} = 7.7\ \text{h}^{-1}$.

groups was observed, but this appeared to be reversible and to not cause permanent framework damage [31].

3.2. Methyl bromide conversion

Blind tests using 10% MeBr in He (10 Nml/min total flow rate) were performed at 400–500 °C in an empty reactor. No product formation was detected. MeBr conversion versus time on stream measured at 300–450 °C, 0.1 bar MeBr, and a 100 Nml/min total flow rate is shown in Fig. 8. Catalyst activation with propene had the same effect on MeBr conversion as was previously observed for MeCl (Fig. 1); the initial conversion increased, and the induction period observed for the non-preactivated catalyst was removed (Fig. 8). As observed for MeCl, an increase in temperature led to higher initial conversion, a shift in initial product selectivity toward the lighter products, and more rapid deactivation.

MeBr conversion versus time on stream curves obtained at 300–450 °C, 0.1 bar MeBr, and a 10 Nml/min total flow rate are shown in Fig. 9. Again, the initial activity increased and the catalyst deactivated more rapidly with increasing temperature. Product selectivities versus time on stream at 450 °C are shown in Fig. 10. The selectivity shifted toward lighter products with increasing time on stream. The same effect was observed at all temperatures, in line with that observed for MeCl (Fig. 4).

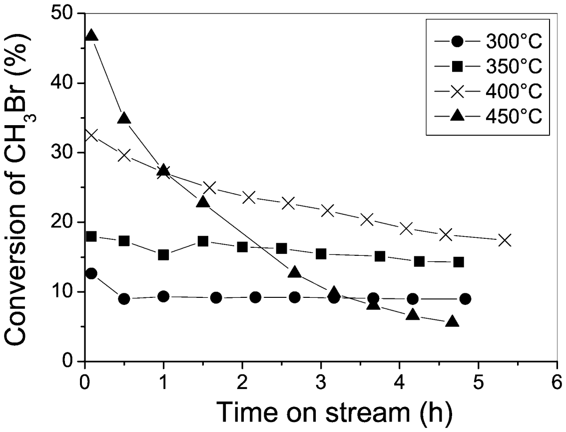

Fig. 9. MeBr conversion versus time on stream at 300–450 °C over SAPO-34, 0.1 bar MeBr, 10 Nml/min, $\text{WHSV}_{\text{eq}} = 0.8\ \text{h}^{-1}$.

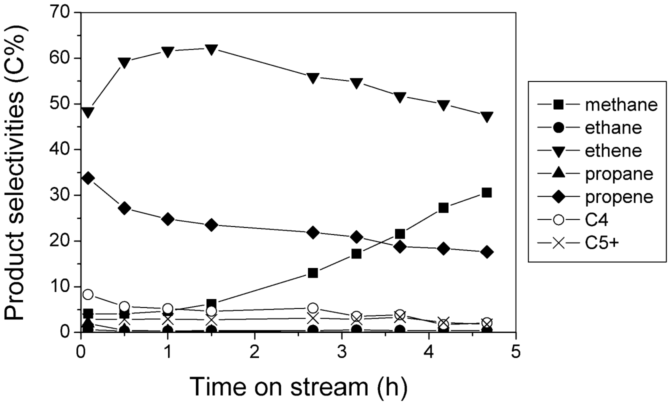

Fig. 10. Product selectivities versus time on stream at 450 °C over SAPO-34, 0.1 bar MeBr, 10 Nml/min, $\text{WHSV}_{\text{eq}} = 0.8\ \text{h}^{-1}$.

Comparing the tests presented in Fig. 8 with those in Fig. 9, which correspond to a 10-fold decrease in feed rate, does show an increase in conversion (although less than 10-fold) when the feed rate was reduced at all temperatures investigated. A very similar result was also obtained for MeCl in Figs. 1 and 3. Product selectivities after 1 h on stream for the two feed rates tested are shown in Fig. 11. It is interesting that the conversion level had little effect on initial product selectivities in the temperature range of 350–450 °C. The same observation was made for MeCl earlier (Fig. 2). Comparing conversion versus time on stream curves obtained at both feed rates for MeBr and MeCl shows that the reactivity of these two reactants was very similar, with possibly slightly lower initial conversion and slightly more rapid deactivation observed for MeBr.

3.3. Formation of halogenated gas-phase products

The formation of halogenated gas-phase products may be of significance. Minimizing the amount of halogenated products will probably be required for any larger-scale application of the conversion of MeX to hydrocarbons. Halogenated compounds (predominantly chloroethane and 2-chloropropane from MeCl and, analogously, bromoethane and 2-bromopropane from MeBr) were indeed detectable in the reactor effluent

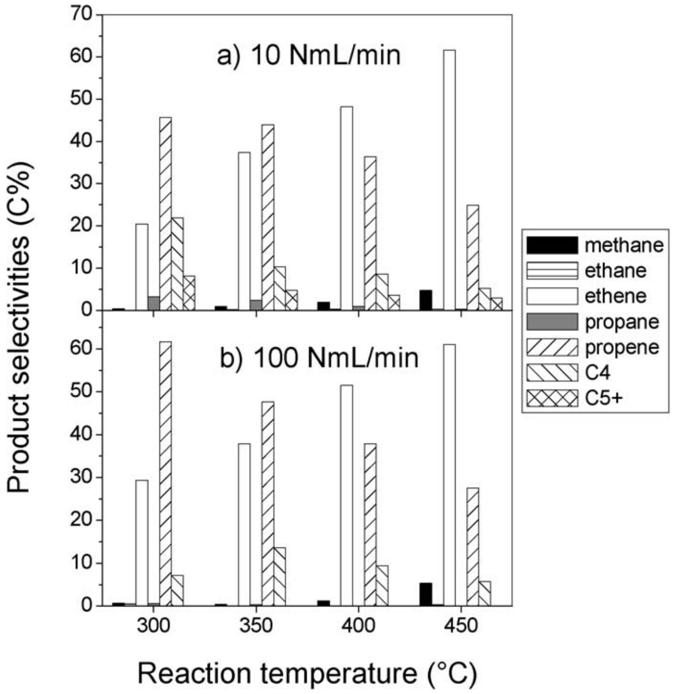

Fig. 11. Product selectivity after 1 h on stream at 300–450 °C over activated SAPO-34. (a) 0.1 bar MeBr, 10 Nml/min, $\mathrm{WHSV_{eq}} = 7.7\ \mathrm{h^{-1}}$; (b) 0.1 bar MeCl, 100 Nml/min, $\mathrm{WHSV_{eq}} = 0.8\ \mathrm{h^{-1}}$.

in the current experiments. The amount of halogenated compounds was analyzed by GC-MS. The added intensities of chloroethane and 2-chloropropane divided by the sum of ethene and propene constitute a fair measure of the content of halogenated compounds, despite the unavoidable differences in the detector response among these molecules. It should be noted that halogenated compounds tend to decompose during chromatographic analysis, as pointed out by White et al. [15]. Based on analyses of neat 2-chloropropane, it can be estimated that about 10% of the 2-chloropropane decomposes into propene and hydrogen chloride during a typical analysis as performed in the present study; however, this amount most likely will depend strongly on the analytical setup used.

In experiments conducted with 1 bar of MeCl (Fig. 5), the above mentioned ratio decreased from 3% to 1.7–0.6% when the reaction temperature was increased from 350 °C to 400–450 °C. Decreasing the pressure from 1 bar to 0.1 bar of MeCl resulted in a drop in the production of chloro compounds by a factor close to five. For MeBr conversion, a similar temperature effect was seen, but at 0.1 bar of MeBr, the yields of halogenated products were quite similar to those found at 1 bar of MeCl, demonstrating that the tendency toward halogenation was greater for MeBr.

It seems plausible that the halogenated compounds are formed by the addition of HX to the alkene double bonds [57]. The observations are in accordance with the thermodynamics of the hydrohalogenation of ethene or propene into 2-halopropane or haloethane [58],

$$\mathrm{HX + CH_2CH_2 \rightarrow CH_3CH_2X}. \tag{7}$$

The decreased yield of halogenated products at lower pressures can be explained simply by the molecularity of the reaction. In addition, the hydrohalogenation reaction of ethene described in Eq. (7) is exothermic [$\Delta_r H^0$ (X = bromine) = −80 kJ/mol; $\Delta_r H^0$ (X = chlorine) = −72 kJ/mol] and entropically disfavored, thus explaining why the percentages of halogenated products decreased with increasing reaction temperature. Finally, relying on the enthalpies and entropies of reaction at standard conditions, the difference in the free energies of reaction was 8 kJ/mol at 323 °C [$\Delta_r G$ (X = bromine) = −1.4 kJ/mol; $\Delta_r G$ (X = chlorine) = +6.6 kJ/mol], corresponding to a factor of 5 in the equilibrium constant at 323 °C. This difference is large enough to explain the differences observed when using MeBr or MeCl as the feed. The values for the free energies indicate that the equilibrium concentrations of haloethane and 2-halopropane will be low, but differences in the kinetics of the hydrohalogenation process between the two reactants cannot be ruled out.

There does not appear to be a clear consensus in the literature on whether or not halogen atoms are incorporated in the hydrocarbons produced when methyl halides are converted over zeolite catalysts. It has been reported that up to 4% of the product from methyl chloride conversion contains halogen [7,11,15,26], in fair agreement with the data presented here, whereas Lersch and Bandermann [13] detected no chlorinated products. Wei et al. did not comment on the yields of chlorinated products in their report on the conversion of methyl chloride over H-SAPO-34 [31].

3.4. *Coreaction of methyl chloride and ethene or propene*

As pointed out in Sections 3.1 and 3.2, the methyl halide conversion increased by a factor close to five on a 10-fold decrease in the feed rate. This deviation from a simple 1:1 proportionality is somewhat unexpected. This type of behavior is often encountered when the reaction products are able to compete with the reactant for the active sites. If this were the case here, then the reactant surface coverage would decrease with increasing conversion, and the concentration and surface coverage of the products would increase, leading to a mismatch between the feed rate and conversion. Recent spectroscopic results by Wei et al. indicate that C=C bonds interact with the active sites of SAPO-34 during MeCl conversion [31].

To investigate whether this site-blocking scenario is valid for methyl halide conversion, the effects of adding 1 NmL/min of ethene or propene to a 10 NmL/min of pure MeCl were investigated at 350 °C. A GC-FID chromatogram displaying the most dominant compounds in the reactor effluent at 1 h on stream is shown in Fig. 12. It appears that adding ethene to the MeCl feed had a negligible effect on propene production, whereas adding propene led to a significant reduction in the ethene yield, as would be expected if the above hypothesis were correct. Moreover, this effect is seen mainly for propene, which has the highest heat of adsorption and is thus most efficient in the competition for sites on the surface. Accurately analyzing these results is obviously difficult without using isotopically la-

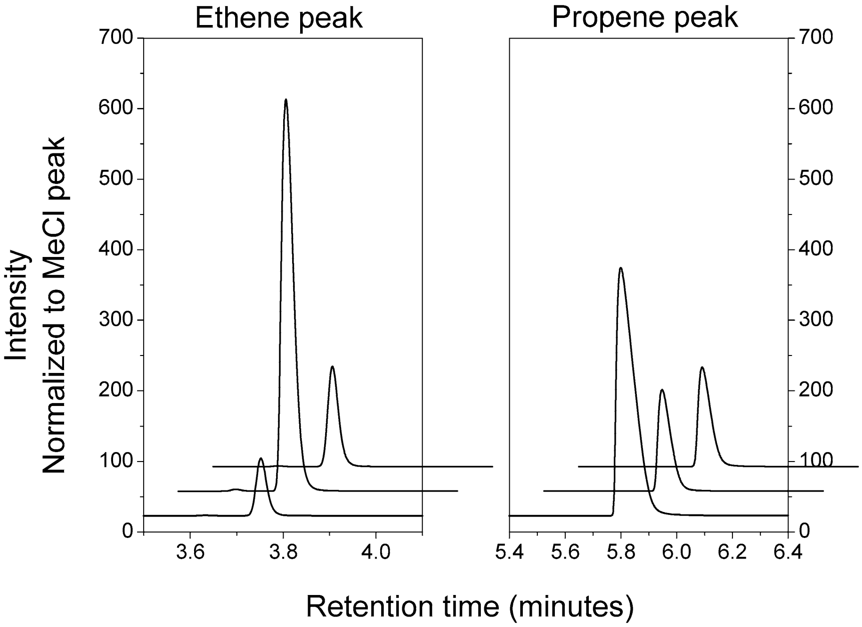

Fig. 12. GC-FID chromatograms normalized to the MeCl peak. 10 NmL/min pure MeCl reacted over 100 mg SAPO-34 catalyst. Back line: without alkene co-feed; middle line: with 1 NmL/min ethene added; front line: with 1 NmL/min propene added.

beled reagents, but if we assume that all products were formed exclusively from MeCl, then the addition of ethene led to a decrease in MeCl conversion from 15 to 12%, whereas the MeCl conversion was 7% in the presence of propene (all values at 1 h on stream). It should be noted, however, that both alkenes displayed significant reactivity when the MeCl stream was replaced by He, with 20% propene conversion and 5% ethene conversion at 1 h on stream.

3.5. *Hydrocarbon deposits in the catalyst*

Thermogravimetric determination of total coke content in the catalyst was performed after activation and testing with MeCl or MeBr at 350, 400, and 450 °C. The thermogravimetric results are presented in Table 1, and selected GC-MS total ion chromatograms for the extracted hydrocarbon deposits are shown in Figs. 13–15.

Already after propene activation, significant amounts of hydrocarbon deposits were present in the catalyst at 350 °C (2 wt%) and 450 °C (9 wt%). The amount of propene added amounted to 34 wt% of the catalyst amount. The GC-MS chromatograms of the coke extracts from the samples activated with propene at 350 and 450 °C, respectively, but not subjected to a reactant feed are compared in Fig. 13. Both samples contained appreciable amounts of methylbenzenes, albeit in much smaller amounts for the sample activated at 350 °C. As mentioned in the Introduction, methylbenzenes have been shown to be the major reactive intermediates in the hydrocarbon pool mechanism for the conversion of methanol to hydrocarbons. In addition, the 450 °C sample contained significant amounts of naphthalene and methyl-substituted naphthalenes, whereas the 350 °C sample contained only traces of polyaromatics. It was previously shown that polyaromatics such as naphthalene have much lower reactivity for the MTH reaction than methylbenzenes [59]. The GC-MS and thermogravimetric data demonstrate that the initial states of the catalyst depend strongly on the temperature at which activation with propene is conducted.

Adding a pure MeCl (10 Nml/min) feed at 350 °C and 450 °C for 1 h after activation significantly enhanced the amount of hydrocarbon deposition in the catalysts, as determined thermogravimetrically (Table 1). The coke content was slightly higher at the higher reaction temperature (14% vs. 12 wt%). The total coke amounts present in the activated and unactivated catalysts were very similar; at 350 °C, the activated sample contained 11.6 wt% coke, whereas the unactivated sample contained 10.0 wt%. The two samples had identical

Table 1
Coke content in activated and used SAPO-34 catalyst. 10 Nml/min feed flow, 100 mg catalyst, no quartz dilution

Reaction temperature (°C)	Activation	Reactant gas	Test duration[a] (min)	Coke amount (wt%)
350	20 Nml propene	No	–	2.0 ± 0.4
350	20 Nml propene	MeCl (pure)	60	11.6
350	No activation	MeCl (pure)	60	10.0
450	20 Nml propene	No	–	8.5
450	20 Nml propene	MeCl (pure)	60	14.3
450	No activation	MeCl (pure)	60	14.3
450	20 Nml propene	MeCl (pure)	5 test cycles, 200 mg_{cat}/ 250 min	20.5
350	20 Nml propene	No	–	2.0 ± 0.4
350	20 Nml propene	MeCl (10%)	10	2.4
350	20 Nml propene	MeCl (10%)	30	2.8
350	20 Nml propene	MeBr (10%)	10	2.4
350	20 Nml propene	MeBr (10%)	30	2.7

[a] In all experiments involving propene activation, the reactor temperature was adjusted to the reaction temperature and left for 10 min after propene injection, before either quenching, dissolving and analyzing, or adding the reactant gas, as in an ordinary test.

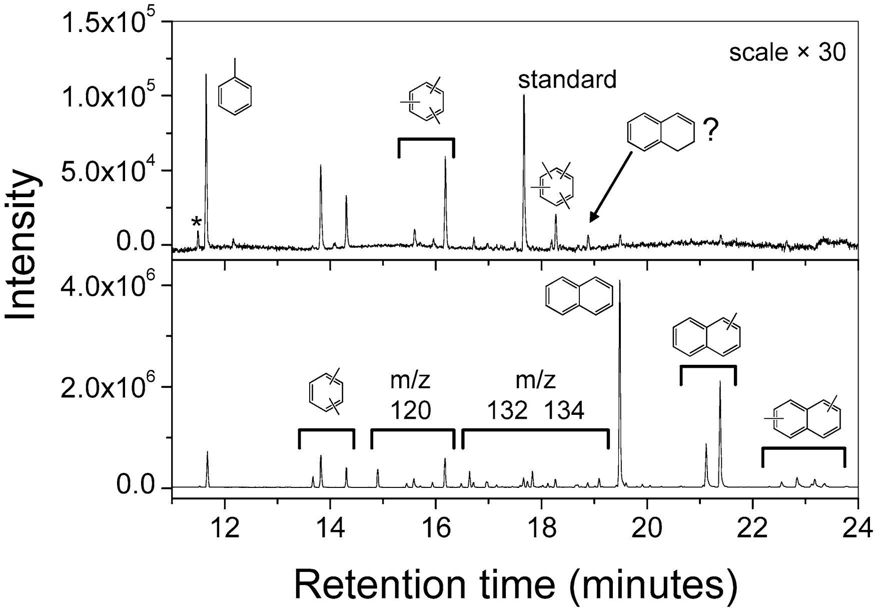

Fig. 13. GC-MS chromatograms of samples activated with propene at 350 °C (top) and 450 °C (bottom), but not subjected to a reactant feed. Note the scale difference. The asterix indicates a solvent impurity. The peaks in the retention time range from 14.8–16.6 ($m/z = 120$) correspond to trimethylbenzene and ethyl-methylbenzene isomers. A mass to charge ratio of 134 corresponds to tetramethylbenzenes and structural isomers, whereas compounds with $m/z = 132$ are suggested to be tetrahydronaphthalene or methylindane isomers by the NIST library search.

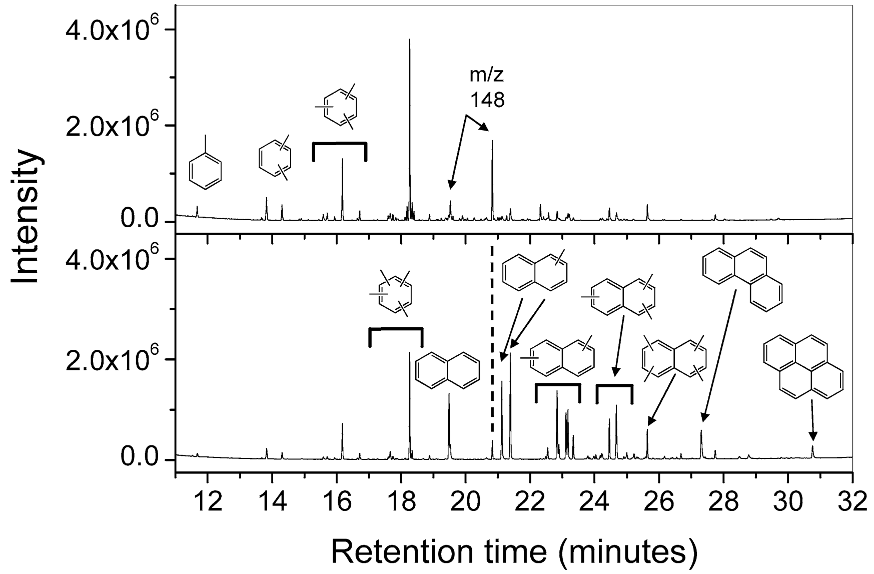

Fig. 14. GC-MS chromatograms of samples subjected to 10 mL/min pure MeCl for 1 h; at 350 °C with activation (top) and at 450 °C with activation (bottom). A mass to charge ratio of 148 corresponds to pentamethylbenzenes and structural isomers. There is an overlap with one of the $m/z = 148$ peaks with the naphthalene signal.

coke content at 450 °C. The GC-MS chromatograms for the activated samples after 1 h on stream prepared at both temperatures are shown in Fig. 14. After being exposed to MeCl for 1 h at 350 °C, the material retained inside the catalyst cages was dominated by methylbenzene isomers. At 450 °C, methyl-substituted naphthalenes were dominant, and higher polyaromatic compounds, such as phenanthrene and pyrene, were detected in appreciable amounts.

An example of the material retained in a severely deactivated sample is shown in Fig. 15. The chromatogram is dominated by methyl-substituted naphthalenes, phenanthrene, pyrene, and methylpyrene. Based on the different reaction temperatures and levels of deactivation of the samples presented in Figs. 13–15, it seem reasonable to conclude that during the lifetime of the SAPO-34 catalyst, a continuous shift occurs in the distribution of the material trapped in the cages. At low reaction temperatures/deactivation levels, the catalyst contained mainly methylbenzenes, which are known to be very active intermediates in the hydrocarbon pool mechanism. At intermediate reaction temperatures/deactivation level, the samples contained larger amounts of naphthalene derivates, which are known to be less active in the hydrocarbon pool mechanism. At the very high-

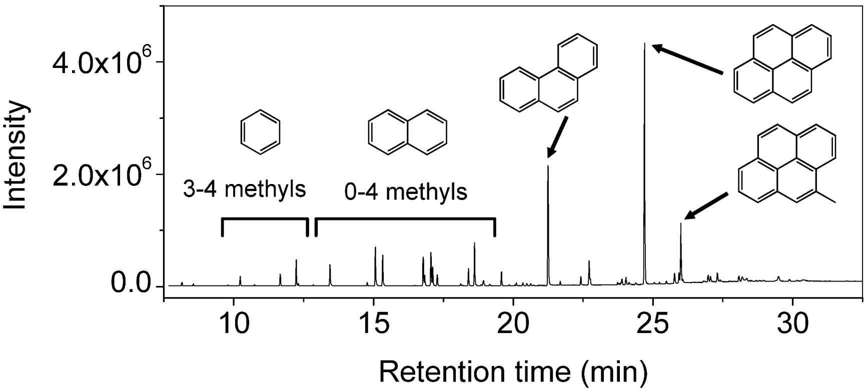

Fig. 15. GC-MS chromatogram of severely deactivated SAPO-34 sample after 5 cycles of MeCl conversion at 450 °C. Reaction conditions as in Fig. 6.

est reaction temperatures/deactivation level, the catalyst voids were filled with heavy, polyaromatic molecules that have much in common with ordinary coke, leading to severe catalyst deactivation.

MeCl conversion for 10 min at 350 °C in a diluted flow (10% MeCl) had no effect on the amount of hydrocarbon deposits in the catalyst compared with the activated catalyst, whereas a slight increase in the amounts of hydrocarbon deposits (i.e., 2.4 vs. 2.8 wt%) was observed after prolonged time on stream (30 min). The amount of hydrocarbon deposits in the catalyst remained the same when using a MeCl or a MeBr feed under the same conditions at 350 °C. These observations are in agreement with the results from the GC-MS analyses of the coke extracts, which are very nearly identical for all of these samples, independent of the nature of the reactant. Indeed, the composition of the retained material is fairly similar to that present after the activation with propene (see the top part of Fig. 13).

It is noteworthy that no halogenated compounds were present among the coke molecules in quantities sufficient to be identified with the spectral search library. The content of halogenated coke can be estimated as <1%, if present at all. Moreover, the composition of the retained material was similar to that described by Arstad and Kolboe in an investigation of the hydrocarbons formed in the SAPO-34 catalyst during the conversion of methanol to hydrocarbons [35,36].

3.6. Methanol conversion

A series of methanol conversion experiments were conducted to obtain data for comparison with the results for the methyl halides. Methanol conversion versus time on stream at 300–450 °C is presented in Fig. 16. The experiments were conducted at reaction conditions nearly identical to those described above for MeCl and MeBr: 0.08 bar of methanol partial pressure and a total flow rate of 100 Nml/min ($WHSV_{eq} = 6.2\ h^{-1}$). At 300 °C, testing was performed with and without activation; in the latter case, an induction period was observed. Close to full conversion was observed already at 350 °C. At 300 °C, the only temperature at which an activity comparison could be made, the initial MeOH conversion over the activated catalyst was 25 times higher than the MeCl conversion obtained under near-identical conditions. One possible explanation for this dramatic difference could be the varying diffusivity among the three reactants. However, the similar conversion rates of MeCl ($M_w = 50$ g/mol, $d_k = 0.41$ nm) and MeBr ($M_w = 94$ g/mol, $d_k = 0.42$ nm), which have similar diameters but widely different molecular weights, compared with the much higher conversion rate of methanol ($M_w = 32$ g/mol, $d_k = 0.38$ nm), indicate that the difference is not due to reactant diffusion limitations but instead might be linked to the lower proton affinities (indicating lower heats of adsorption and thus lower surface coverages) of MeCl and MeBr compared with MeOH (647, 664, and 761 kJ/mol, respectively [60]). This notion is supported by theoretical calculations reported previously [45]. Recent results from Wei et al. [31] may offer an additional explanation for the low conversion of methyl halides compared with methanol. Using Fourier transform infrared spectroscopy, these authors found that the production of HCl during MeCl conversion over SAPO-34 led to the formation of P–OH groups, which disappeared after evacuation. They suggested that HCl may break Al–O–P bonds in the catalyst, leading to the formation of AlCl and inactive P–OH [31].

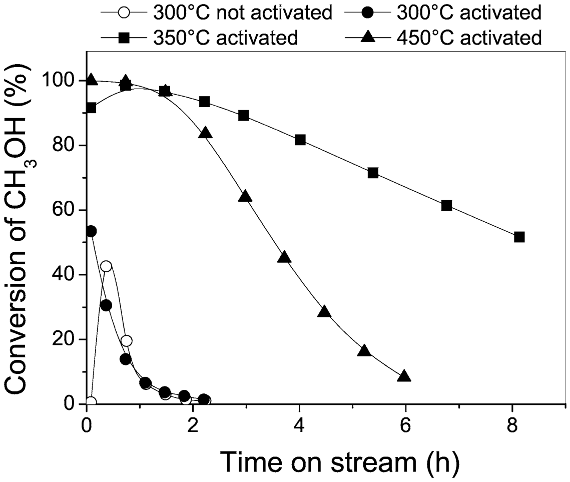

Fig. 16. MeOH conversion versus time on stream at 300–450 °C over SAPO-34, 0.08 bar CH_3OH, 100 Nml/min, $WHSV_{eq} = 6.2\ h^{-1}$.

During the MeOH tests, rapid deactivation was observed at all temperatures. Integrating the methanol conversion curve obtained at 300 °C indicates that the catalyst converted 12.4 mmol of methanol during its lifetime. In comparison, 3.8 mmol of methyl chloride was converted during the first 8 h on stream at 300 °C under near-identical reaction conditions, but without visible loss of catalytic activity (Fig. 1).

Product selectivities after 5 min on stream are shown in Fig. 17. A shift toward lighter products occurred with increasing temperatures. Product selectivities versus time on stream at 450 °C are shown in Fig. 18. As for the MeCl and MeBr tests above, a selectivity shift occurred with time on stream.

Because the deactivation rate differs for the methyl halides and methanol, product selectivities were compared after extrapolation to 0 time on stream. Although extrapolation always introduces some uncertainty, this approach provides the only way to compare the experimental data decoupled from the effects of deactivation. Extrapolated product selectivity patterns for all experiments are listed in Table 2. The extrapolation was performed by drawing a straight line between the first two data points for each product in a selectivity versus time-on-stream plot and extrapolating the line to 0 time on stream.

It is interesting to note that at similar reaction conditions, the initial product selectivities were very similar for MeCl, MeBr, and MeOH conversion, despite the much higher conversion rate

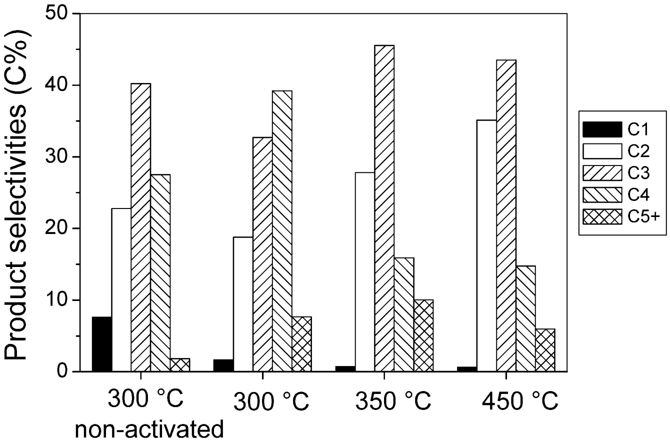

Fig. 17. Product selectivities after 5 min on stream at 300–450 °C over SAPO-34, 0.08 bar CH_3OH, 100 Nml/min, $WHSV_{eq} = 6.2\ h^{-1}$.

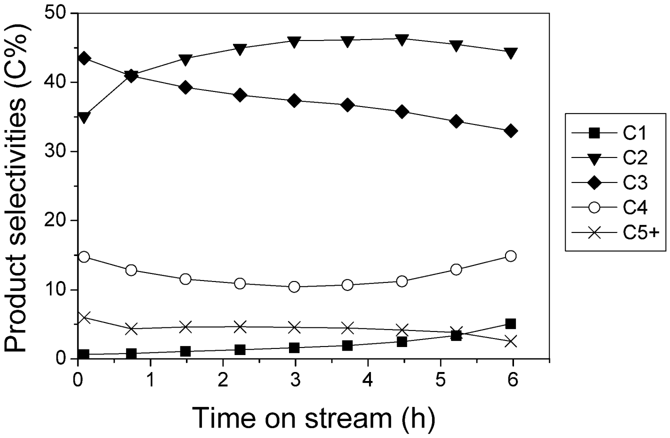

Fig. 18. Product selectivities versus time on stream at 450 °C over SAPO-34, 0.08 bar CH_3OH, 100 Nml/min, $WHSV_{eq} = 6.2\ h^{-1}$.

Table 2
Product selectivities (%) extrapolated to zero time on stream

Reactant	Partial pressure (bar)	Total gas flow (NmL/min)	Reaction temperature (°C)	Methane	Ethane	Ethene	Propane	Propene	C_4	C_{5+}
MeCl	1.0	10	300	1	0	8	8	34	38	11
MeCl	0.1	10	300	1	0	8	10	47	35	0
MeCl	0.1	100	300	1	0	18	3	50	31	0
MeBr	0.1	10	300	1	0	5	8	49	31	8
MeBr	0.1	100	300	0	0	6	1	65	26	0
MeOH	0.08	100	300	2	N/A[a]	17		30	44	8
MeCl	1.0	10	350	0	0	16	6	30	31	17
MeCl	0.1	10	350	1	0	21	11	42	25	0
MeCl	0.1	100	350	1	0	29	1	50	20	0
MeBr	0.1	10	350	2	0	25	7	44	16	7
MeBr	0.1	100	350	2	0	29	1	52	18	0
MeOH	0.08	100	350	1		28		45	15	11
MeCl	1.0	10	400	0	1	21	7	36	28	7
MeCl	0.1	10	400	1	0	34	4	41	17	4
MeCl	0.1	100	400	2	0	35	1	47	17	0
MeBr	0.1	10	400	2	0	37	5	39	12	5
MeBr	0.1	100	400	2	0	45	0	46	7	0
MeOH	0.08	100	400	N/A[b]						
MeCl	1.0	10	450	2	1	25	8	38	21	6
MeCl	0.1	10	450	2	1	41	4	37	12	4
MeCl	0.1	100	450	1	0	41	1	46	11	0
MeBr	0.1	10	450	4	0	45	3	35	9	4
MeBr	0.1	100	450	2	0	49	0	38	10	0
MeOH	0.08	100	450	1		34		44	15	7

[a] Ethane/ethene and propane/propene were not chromatographically separated in the MeOH experiments.

[b] This experiment was not conducted.

of methanol, particularly at and above 350 °C. Such similarities in product distributions over SAPO-34-type catalysts were previously proposed to be an effect of an equilibration of olefinic products within the cages [51]. Further work is in progress to gain further insight into the specifics of methyl halide conversion over SAPO-34 catalysts.

4. Conclusion

The results obtained in this study show that the conversion of methyl chloride and methyl bromide to olefins over H-SAPO-34 bears a strong resemblance to the more widely studied methanol to olefins reaction. The induction period (which may be overcome by propene activation), the product distribution, and hydrocarbon deposits in the catalyst are all indications of a mutual reaction mechanism. The conversion levels of methyl chloride and methyl bromide were similar, whereas that of methanol was 25 times higher. The H-SAPO-34 catalyst endured several methyl chloride reaction–regeneration cycles at 450 °C. Our findings indicate that H-SAPO-34 is an active, selective, and structurally stable catalyst for the conversion of methyl chloride to olefins.

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