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Catalysis Today 63 (2000) 355–362

CATALYSIS TODAY

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Non-oxidative reaction of $CBrF_3$ with methane over NiZSM-5 and HZSM-5

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Abstract

Catalytic hydrodehalogenation of $CBrF_3$ with methane was studied over NiZSM-5 and HZSM-5 in tubular reactor between 573 and 873 K and at ambient pressure. It was found that the incorporation of nickel into HZSM-5 significantly enhanced the activity of the zeolite. A variety of products were formed during reaction, including CH_3Br, CHF_3, CH_2Br_2, C_2F_6, C_2H_4, C_2H_2, $C_2H_2F_2$, $CHBrF_2$, CH_2BrF, and C_2H_3Br. XRD analysis showed that these two zeolite catalysts did not suffer any loss in their crystallinity during use. Deactivation of both NiZSM-5 and HZSM-5 may, in part, be due to poisoning of the zeolite by halogens. Coking is another cause of the deactivation of HZSM-5, but appears to play a minor role in NiZSM-5 deactivation. A series of methylated silicone oils was detected during reaction over NiZSM-5. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: NiZSM-5; HZSM-5; Halon 1301; $CBrF_3$; Methane; Hydrodehalogenation

1. Introduction

Stratospheric ozone depletion has been linked to anthropogenic emission of Cl- and Br-containing compounds [1,2]. These findings led to the 1987 Montreal protocol and its subsequent revisions in London in 1990 and Copenhagen in 1992, resulting in a phase-out of the production of halons (bromine containing fluorocarbons and chlorofluorocarbons (CFCs)) by 1 January 1994 and of CFCs by 1 January 1996 [3]. The major consequences of the phasing out of halons and CFCs have been the initiation of an exhaustive effort to develop new drop-in replacements, and the need to develop effective halon and CFC treatment processes.

Halon and CFC destruction options currently in development include a range of thermal, chemical, biological and electrical processes. With the exception of thermal processes, other technologies are still at a preliminary level of development [4–7]. Thermal incineration, currently an established treatment technology, converts CFCs and halons into carbon dioxide and hydrogen halides through high temperature hydrolysis in the presence of excess oxygen. However, the combustion inhibition properties of halons make incineration a very unattractive disposal option from an energy consumption perspective. Moreover, emission of corrosive and hazardous halogen acids (HF, HCl, HBr) and free halogen molecules (F_2, Cl_2, Br_2) and toxic products of incomplete combustion (PIC) during the incineration process have inhibited its wide-scale acceptance [8]. In order to reduce incineration temperatures and thus reduce the cost in fuel consumption, catalytic destruction of CFCs has been investigated [4–7]. However, the development is still at bench scale level, as catalyst deactivation remains an unresolved problem in the development of this technology. Recently, another new technology,

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PII: S0920-5861(00)00479-X

plasma arc pyrolysis process, has been commercialized, which utilizes the extremely high temperatures (10,000 K, or more) to pyrolyze toxic substance into atomic or ionic form. Subsequent down-stream treatment converts these atoms into simple environmentally benign molecules. The operating cost of this process, however, is estimated to be up to five times higher than conventional thermal incineration [8].

Along with the exhaustive search for halon and CFC replacements, conversion as a treatment technology has attracted considerable research interest, where the general focus is to convert halons or CFCs into products of economic value. Hydrodehalogenation is a non-oxidative process, in which CFCs or halons react with hydrogen or hydrogen donors in the gas phase or catalytically. There are relatively few studies of homogeneous gas-phase hydrodehalogenation of CFCs and halons, in which chlorine and bromine are successfully replaced by hydrogen or hydrogen donor species [9–12]. However, catalytic hydrodehalogenation can achieve conversion of CFCs and halons under relatively mild conditions, and allow enhanced control of product selectivity. Catalytic reaction of CFCs, CCl_2F_2, in particular, with hydrogen over metal or supported metal catalysts has been extensively studied [13–26], but there are apparently no corresponding studies of halon reactions. We have recently reported the hydrodebromination of halon 1301 ($CBrF_3$) with methane over transition metal (Cu, Mn and Co) exchanged ZSM-5 zeolite catalysts, and found CHF_3 and CH_3Br were two major products between 673 and 873 K [27].

This paper presents the results of a more detailed study of the reaction of halon 1301 ($CBrF_3$) and methane over NiZSM-5, and compares the activity of NiZSM-5 with HZSM-5. Nickel exchanged HZSM-5 zeolite has been previously reported to be active in the hydrogenolysis of halogenated aliphatic hydrocarbons [28,29]. Methane was used as a hydrogen source instead of molecular hydrogen. In addition to its availability at low cost, methane has other potential advantages over hydrogen. For example, molecular hydrogen is easily ignited and presents considerable hazards when used in large scale because of its low molecular weight and high diffusibility [30]. It is also possible to minimize the production of the mineral acids HF and HBr through reaction of $CBrF_3$ with CH_4, as shown in our previous studies [27].

2. Experimental

The experimental facility used in this study has been described in detail elsewhere [31]. Briefly, the apparatus used was a plug flow high-purity alumina reactor with an exit line comprising of a liquid trap (273 K), caustic scrubber (0.1 M, NaOH), on-line micro GC (MTI) equipped with molecular sieve 5A and Poraplot U columns, and GCMS (Shimadzu QP5000) equipped with an AT-Q column. Quantitative analysis of CHF_3, CH_3Br and all hydrocarbons was achieved by using experimentally obtained relative molar response (RMR) factors for TCD detection from standard gases, while for other species, RMR values were estimated from published correlations [31]. Carbon mass balances of 95% (±2%) were routinely achieved. The reactor was operated at a nominal pressure of one atmosphere. Three gases, N_2 (99.99%), $CBrF_3$ (98.5%, 1.5% N_2), and CH_4 (99.97%), were metered with electronic mass flow controllers (Brooks). An equi-molar feed of $CBrF_3$ and CH_4 in a nitrogen diluent was examined with the input volumetric ratio of N_2:$CBrF_3$:CH_4 = 11:1:1. A three-zone electric tube furnace was employed to heat the 7.0 mm i.d. reactor tube.

Zeolite HZSM-5 (Si/Al = 30, 425 $m^2\,g^{-1}$) was provided by Zeolyst International in powder form. A 1 wt.% NiZSM-5 (66% of maximum theoretical exchange limit) was prepared by ion exchange of HZSM-5 with aqueous $Ni(NO_3)_2$ solution at a pH of 1.8, by stirring the mixture for 72 h. Ion exchanged samples were subsequently dried at 393 K for 12 h, and further heated stepwise at 573 K for 2 h and 773 K for 3 h. Catalyst evaluation was undertaken with 500 mg of catalyst, which was pelletized, crushed and sieved to 20–40 mesh prior to charging into the reactor. The catalyst was heated in flowing nitrogen to the desired reaction temperature before introducing a reaction mixture of $CBrF_3$ and CH_4, diluted in nitrogen. Fresh and used catalysts were characterized by X-ray powder diffraction (Siemens D5000, Cu Kα radiation), ^{27}Al and ^{29}Si MAS NMR spectroscopy (Brucker MSL300) and XPS (Kratos XSAM800 instrument, Mg Kα radiation).

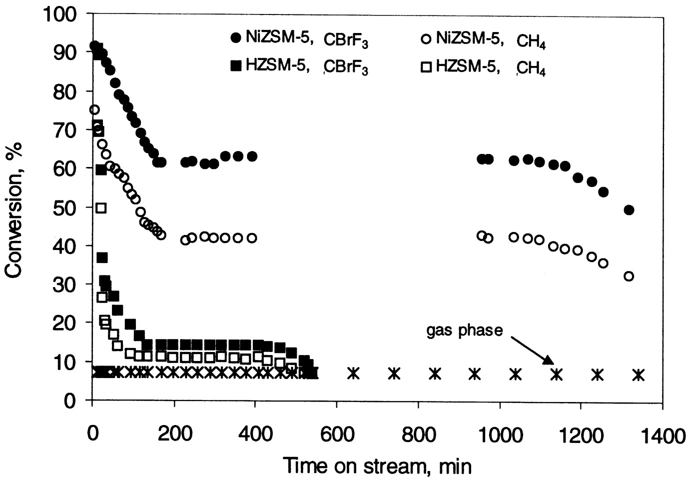

Fig. 1. Conversion of $CBrF_3$ and CH_4 as a function of time on stream at 873 K and 3500 h^{-1} GHSV over NiZSM-5 and HZSM-5 zeolites, compared with the conversion of $CBrF_3$ in gas phase.

3. Results and discussion

Fig. 1 shows conversion of $CBrF_3$ and CH_4 as a function of time on stream at 873 K and at a GHSV of 3500 h^{-1} (based on the total flow rate of gas streams) over zeolite catalysts. Also shown is the corresponding homogeneous gas-phase conversion of $CBrF_3$, which is similar to CH_4 conversion levels at these temperatures and residence times. A more comprehensive analysis of the homogeneous gas-phase reaction is reported elsewhere [31]. A striking feature of the reaction over both zeolite catalysts is the initial high conversion of both $CBrF_3$ and CH_4, which falls rapidly to a lower steady-state level. The steady-state conversion level of $CBrF_3$ over NiZSM-5 lasts approximately 1000 min, after which a second deactivation period is observed, while HZSM-5 activity was maintained for only 400 min, where upon the catalyst deactivates to levels similar to the gas-phase reaction. Conversion levels of both $CBrF_3$ and CH_4 over NiZSM-5 are much higher than in the corresponding gas-phase reaction, while the conversion of $CBrF_3$ and CH_4 is only slightly higher over HZSM-5 compared with gas-phase levels. It is evident that incorporation of nickel into HZSM-5 enhances catalytic activity. In addition, the incorporation of nickel into HZSM-5 suppresses the conversion of CH_4, as the difference between the conversion levels of $CBrF_3$ and CH_4 over NiZSM-5 is significantly larger than that over HZSM-5 and during the gas-phase reaction.

The products detected from the reaction of $CBrF_3$ and CH_4 over NiZSM-5 consist of CH_3Br and CHF_3 as major products and CH_2Br_2, C_2F_6, C_2H_4, C_2H_2, $C_2H_2F_2$, HF, HBr as minor products, with trace quantities of a number of other species such as $CHBrF_2$, CH_2BrF, and C_2H_3Br. In this context we define selectivity of species i, S_i as

$$S_i = \frac{[\text{species}\, i]}{\sum n_i [\text{all carbon-containing product species}]}$$

where n_i denotes the number of carbon atoms in i.

Fig. 2 shows the selectivity (based on carbon-containing products) of CH_3Br, CHF_3, CH_2Br_2, C_2F_6, C_2H_4, C_2H_2, and $C_2H_2F_2$ as a function of time on stream at 873 K and 3500 h^{-1} (GHSV) during the reaction over NiZSM-5. Other products, produced at a selectivity of less than 0.5%, are not included.

Over NiZSM-5, CH_3Br, and CHF_3 are the two major products of the reaction, although the selectivity to CH_3Br is consistently higher than that of CHF_3. This is in contrast to the gas-phase reaction, where CHF_3 is produced in excess of CH_3Br [31]. The selectivity to CH_3Br decreases as the catalyst deactivates, while CHF_3 selectivity increases. Another notable feature is the relatively high selectivity to CH_2Br_2 and C_2F_6, which are only produced in trace quantities during

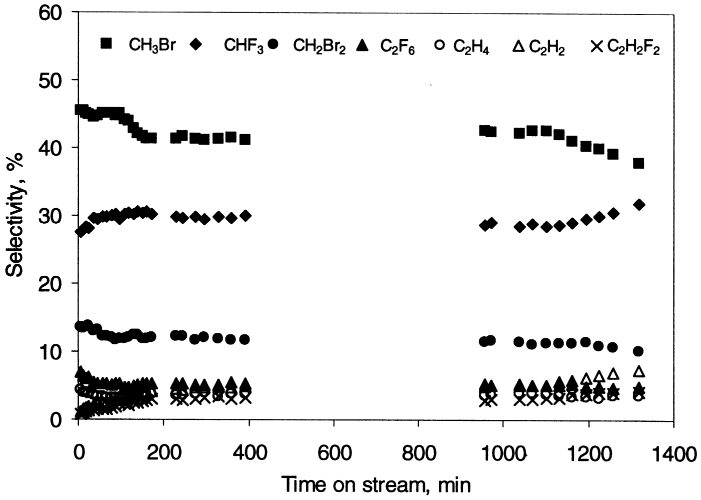

Fig. 2. Product selectivity as a function of time on stream at 873 K and 3500 h^{-1} GHSV over NiZSM-5 zeolite.

gas-phase reaction. Selectivity to C_2H_4, C_2H_2, and $C_2H_2F_2$ are similar (at 4%) once steady-state reaction is achieved. However, the production of C_2H_2 and $C_2H_2F_2$ increases during the deactivation of NiZSM-5, while C_2H_4 production shows the reverse trend.

Selectivity as a function of time on stream at 873 K and 3500 h^{-1} over HZSM-5 is presented in Fig. 3. As over NiZSM-5, the production of CH_3Br is favored over CHF_3 until after 500 min time on stream, where CHF_3 selectivity becomes higher than CH_3Br. This coincides with the deactivation period of HZSM-5, where conversion levels decrease to gas-phase levels. One striking feature of the reaction observed over HZSM-5 is the high selectivity to C_2F_6, which is formed at very low quantities over NiZSM-5 and only in trace amounts during the gas-phase reaction [31]. The production of C_2H_4 and $C_2H_2F_2$ displays similar

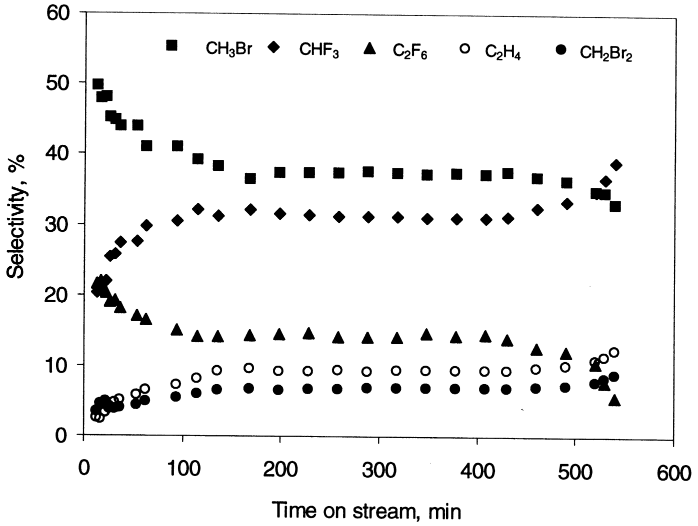

Fig. 3. Product selectivity as a function of time on stream at 873 K and 3500 h^{-1} GHSV over HZSM-5 zeolite.

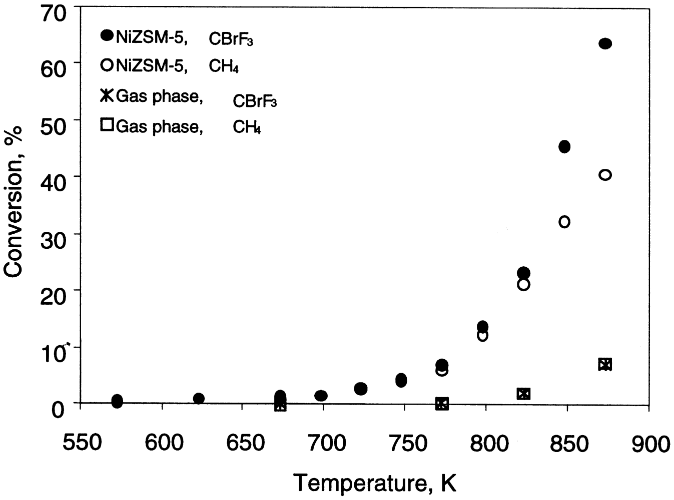

Fig. 4. Conversion of $CBrF_3$ and CH_4 as a function of temperature at a GHSV of 3500 h^{-1} over NiZSM-5 zeolite and in gas phase (the corresponding space time is approximately 1 s).

behavior to that over NiZSM-5, although the production of C_2H_4 is not favored initially over HZSM-5. Little C_2H_2 was detected over HZSM-5, but was produced at a selectivity of approximately 5% over NiZSM-5.

The conversion of $CBrF_3$ and CH_4 over NiZSM-5 as a function of temperature is plotted in Fig. 4. For this purpose, the steady-state conversion after 180 min on stream was chosen.

It can be seen from Fig. 4 that at low temperature ($<$750 K), there is little difference between conversion levels of $CBrF_3$ and CH_4, while at higher temperatures, the conversion of $CBrF_3$ is higher than that of CH_4, and this feature becomes more pronounced with increasing temperature. This suggests that the reaction pathway at high temperature is more complex than that predicted for the simple 1:1 stoichiometry of reaction (1).

$$CBrF_3 + CH_4 \rightarrow CHF_3 + CH_3Br \qquad (1)$$

The conversion behavior is similar to that observed in gas-phase reaction, although for comparable conversion levels, the required reaction temperature is much higher for the gas-phase reaction. Gas-phase reaction commences at about 773 K, and increases dramatically with temperature, and above 900 K, the conversion of $CBrF_3$ starts to exceed that of CH_4 [31]. In comparison with the reaction over HZSM-5 and in gas phase, NiZSM-5 enhances the difference in conversion levels of $CBrF_3$ and CH_4.

At low temperatures ($<$700 K) (and low conversion levels), the major reaction products detected were CH_3Br and CHF_3, in conformity with reaction (1). Above 700 K, however, the selectivity to CH_3Br declines and other reaction products appear, such as CH_2Br_2, C_2H_4, C_2H_2, $C_2H_2F_2$, and C_2F_6, presumably due to secondary reaction of CH_3Br and to a smaller extent, CHF_3. Under these conditions, selectivity to CHF_3 decreases, while selectivity to C_2F_6 and $C_2H_2F_2$ increases with temperature. In corresponding gas-phase reaction [31], at low temperatures, CHF_3 and CH_3Br are two major products and account for more than 80% of all products. In the gas phase, the selectivity to CHF_3 increases up to 1023 K, while CH_3Br decreases. Among minor products of $C_2H_2F_2$, C_2H_4, C_2H_2, and C_2H_3Br, selectivity to C_2H_4 is highest below 1000 K, while above this temperature, $C_2H_2F_2$ is mostly favored. As in the gas-phase reaction, secondary products appear to form through decomposition of the initial products CH_3Br and CHF_3. As expected, the conversions of both $CBrF_3$ and CH_4 decrease with increasing space velocity. With the decrease in conversion of $CBrF_3$ and CH_4, the selectivity to CH_3Br increases, consistent with the gas-phase

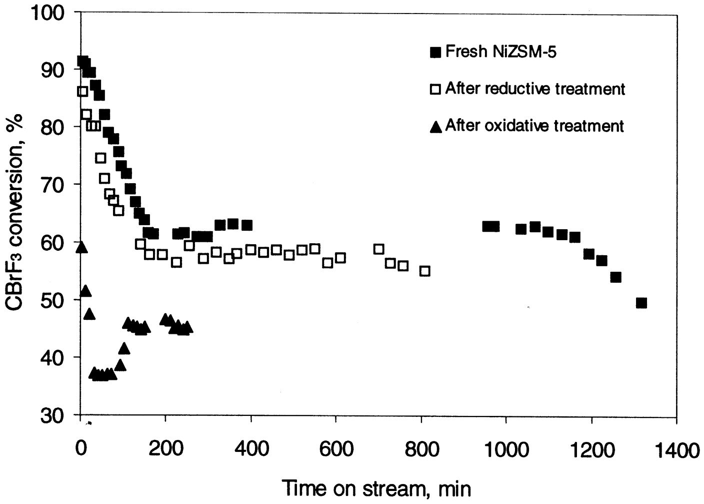

Fig. 5. The effect of hydrogen and oxygen treatment on the catalyst activity as a function of time on stream at 873 K and 3500 h^{-1} GHSV over NiZSM-5 zeolite.

CH_3Br formation profile [31]. Over NiZSM-5, the selectivity to CHF_3 declines slightly with GHSV, while in gas phase, it increases significantly. Among the minor products produced, CH_2Br_2, C_2H_4, C_2H_2, and C_2F_6 are favored at low space velocity, which is similar to gas-phase reaction selectivity. However, $C_2H_2F_2$, is favored at high space velocity, which is opposite to that for the gas-phase reaction [31].

Both zeolite catalysts show a high initial activity for conversion of $CBrF_3$ and CH_4, but HZSM-5 quickly deactivates to an initial steady-state level after 130 min. NiZSM-5, on the other hand, deactivates at a slower rate and achieves stead-state conversion level after approximately 180 min on stream. Analysis of the spent catalyst samples by X-ray diffraction showed there was no loss in crystallinity after 1200 min on stream for NiZSM-5 and 540 min for HZSM-5. Thus, the inherent structure of the catalysts did not change significantly during this period, and thus loss of activity is not due to collapse of the zeolite structure.

In order to investigate possible explanations for the loss of activity of the zeolites, deactivated NiZSM-5 and HZSM-5 samples were treated in an oxygen stream at up to 623 K for 3.5 h, and their resulting activity re-examined. These results are displayed in Figs. 5 and 6. Spent NiZSM-5 did not recover its original activity after oxygen treatment. Furthermore, the initial conversion of $CBrF_3$ rapidly dropped from about 60 to 37%, then increased to a steady-state level of approximately 45% after 80 min which is approximately 65% of its original activity. This is considerably lower than the conversion level achieved after treatment with hydrogen. These observations suggest coking is a minor contributor to deactivation of NiZSM-5. The initial low activity of oxygen treated NiZSM-5 is probably due to oxidation of nickel to nickel oxide, similar to observations made by others, that metal-oxide impregnated ZSM-5 zeolites have fewer acid sites compared with their corresponding metal-ZSM-5 zeolites, and thus have lower activity. With time on stream in the presence of methane, nickel oxide formed in NiZSM-5 may be reduced by methane, thus restoring its original activity. However, HZSM-5 was observed to regain most of its initial activity, suggesting coking may be contributing to the deactivation of HZSM-5 (see Fig. 6). This observation is in good agreement with the results obtained by Lersch and Bandermann [32], who studied the decomposition of chloromethane over various metal-exchanged ZSM-5 and HZSM-5, and found that metal sites, such as Mg and Mn, in metal exchanged ZSM-5 can reduce coking in comparison to HZSM-5. However, they claimed that both metals exchanged

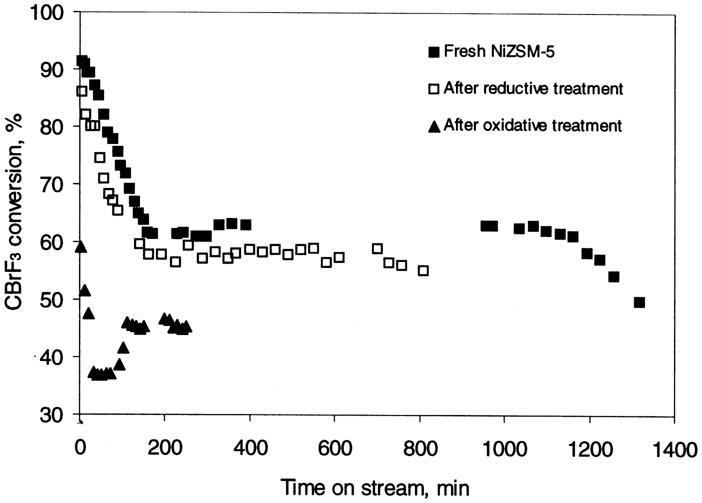

Fig. 6. The effect of hydrogen and oxygen treatment on the catalyst activity as a function of time on stream at 873 K and 3500 h^{-1} GHSV over HZSM-5 zeolite.

ZSM-5 and HZSM-5 can recover their activity after oxidative regeneration.

It has been reported that Rh/SiO_2 catalysts deactivated by chlorine in the hydrodechlorination of trichloroethylene are readily regenerated by flowing hydrogen over the catalyst at 573 K [35]. After treatment in hydrogen for 3 h at 623 K, it is found that NiZSM-5 recovered more than 90% of its initial activity, compared with the fresh catalyst, while HZSM-5 recovered to approximately 60%. Hence, it seems that bromine or fluorine poisoning may be a major contribution to the deactivation of zeolite catalysts. ^{27}Al NMR spectra of spent NiZSM-5 samples revealed the presence of tetrahedral and octahedral Al in spent NiZSM-5 catalysts. However, Lersch and Bandermann reported that MgZSM-5 takes up chlorine during the decomposition of chloromethane, and speculated that chlorine was present in the form of $MgCl_2$, $AlCl_3$ or both, or even that HCl was adsorbed on the surface, as the formation of volatile $FeCl_3$ could be observed when FeZSM-5 was used instead of MgZSM-5 [32].

Trace amounts of $C_6H_{18}O_3Si_3$, $C_8H_{24}O_4Si_4$, and $C_{10}H_{30}O_5Si_5$ silicone oils were trapped and identified by GCMS during the reaction of $CBrF_3$ and CH_4 over NiZSM-5. $C_6H_{18}O_3Si_3$ accounts for more than 95% of these silicone oils, based on GC peak areas. As the structure of the zeolite remained unchanged, it is speculated that the methylation (2) of Si in NiZSM-5 probably only occur in the amorphous state of the zeolite, and is probably a consequence of the catalytic deactivation observed in the reaction of $CBrF_3$ and CH_4 over NiZSM-5 zeolite. No oils were detected during reaction of methane in the absence of $CBrF_3$ over NiZSM-5, or during reactions over HZSM-5.

4. Conclusions

The reaction of $CBrF_3$ with CH_4 is enhanced over NiZSM-5 compared to HZSM-5, producing CH_3Br, CHF_3, CH_2Br_2, C_2F_6, C_2H_4, C_2H_2 and $C_2H_2F_2$ as major products. At low temperatures, there is little difference between the conversion levels of $CBrF_3$ and CH_4, while at higher temperatures, the conversion level of $CBrF_3$ is higher than that of CH_4. Poisoning by halogens is suggested to be the main reason of the deactivation of NiZSM-5, while the effect of coking appears to be minor. The production of CH_3Br and CHF_3 is favored over both NiZSM-5 and HZSM-5, and accounts for more than 70% of all products. However, significant amounts of CH_2Br_2 are formed over NiZSM-5, while over HZSM-5, C_2F_6 is produced at relatively high selectivities. The formation of silicone oils detected during reaction over NiZSM-5 may also contribute to the deactivation of NiZSM-5.

Acknowledgements

Australian Research Council is gratefully acknowledged for financial support of this project. Kai Li is indebted to AusAID for a postgraduate scholarship. Zeolyst International is thanked for providing various ZSM-5 zeolites.

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