

CATALYTIC COUPLING OF HALON 1301 WITH METHANE OVER CUZSMS ZEOLITE

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SUMMARY

This work presents the results of an experimental investigation into the effect of CuZSM5 zeolite on the coupling reaction between Halon 1301 (CBrF₃) and methane in a nitrogen atmosphere over the temperature range of 573 to 873 K, space velocity (GHSV) of 3600h⁻¹-18000h⁻¹, and atmospheric pressure. The catalytic ability of CuZSM5 is dependent on temperature. There exist two stable periods with increasing time-on-stream. The conversion levels of both CBrF₃ and CH₄ increase with increasing temperature and decrease with increasing space velocity. The products consist of CHF₃ and CH₃Br as major products, and C₂H₄, C₂H₂, C₂H₂F₂, CHBrF₂, CH₂BrF, CH₂Br₂, C₂F₄, C₆H₅, C₆H₅Br, C₆H₅F and C₂H₆ as minor products.

INTRODUCTION

Bromine and/or chlorine containing fluorocarbons, which are known as halons, have a variety of important industrial applications, especially used as firefighting agents. However, they have photochemical sources of Br and Cl atoms, and it is this property that has been shown to be detrimental to stratospheric ozone concentration. Therefore, continued production and use of halons have been curtailed [1]. The treatment of excess amounts of such compounds then presents another serious environmental issue. The main advantages of catalytic treatment compared with other decontamination technologies can be summarized as follows: high efficiency at very low pollutant concentrations, low energy consumption, small size of the depuration unit, very low production of secondary pollutants, and allowing control over the selectivity of useful products [2].

Extensive studies have been concentrated on catalytic treatment of chlorine containing fluorocarbons (CFC) and chlorohydrocarbons. Bozzelli et al. studied the catalytic hydrodechlorination of 1,2-dichloroethane and trichloroethylene over Rh/SiO₂ catalysts, and proposed a detailed reaction scheme to explain the product formation [3]. Coq et al. investigated the conversion of dichlorodifluoromethane over Pd black and Pd supported on alumina, graphite, or AlF₃, and found that the selectivity of the reaction slightly depended on the size of the Pd particles and the nature of the support [4]. Coq et al. also investigated catalytic conversion of dichlorodifluoromethane over bimetallic palladium catalysts, and concluded that the product selectivities were partly dependent on the CCl₂F₂ pressure. Dhandapani and Oyama synthesized a series of supported and unsupported metal carbide catalysts to study the selective dehalogenation of CFC₁₂ (CCl₂F₂) and observed that the unsupported carbides have lower initial conversion than the supported carbides and the only product formed was CH₂F₂ [5].

There is little reporting on the catalytic hydrodehalogenation of halons. In this work, we presented some results about the catalytic coupling reaction of Halon 1301 (CBrF_3) with methane on CuZSM5 zeolite.

EXPERIMENTAL

Catalysts Preparation

HZSM5 of different mole ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ were provided by Zeolyst International in powder form. The CuZSM5 ($\text{SiO}_2/\text{Al}_2\text{O}_3=150$, 2.0wt%) catalysts were prepared by ion exchange of HZSM5 with aqueous $\text{Cu}(\text{NO}_3)_2$ solution. At 1.83 of pH value and ambient atmosphere, the mixture solution was stirred for 72 hrs, then filtered and washed. The samples were dried at 120°C for 12 hrs and stepwise calcined afterwards at 300°C for 2 hrs and 500°C for 3 hrs. The obtained CuZSM5 was then pressed, crushed, and sieved into 20-40 mesh particles.

The experimental facility and catalyst testing procedures have been described in detail elsewhere [6]. Briefly, the catalytic evaluation of Halon 1301 in a nitrogen bath gas was studied at normal atmosphere in 7.0mm i.d. alumina plug flow reactor. A high purity (99.99%) alumina reactor rather than quartz reactor was used because the quartz tube is rapidly corroded by fluorides at high temperature. The reactor was heated in a three-zone electric tube furnace. This design allows for improved temperature control, and temperature profiles across a 5-cm zone can be controlled to within 5 K in the reaction zone of the furnace. Feed gases CBrF_3 (98.50%), CH_4 (99.97%), and N_2 (99.99%) were metered with electronic mass flow controllers.

The reactor effluent was analyzed on a MTI micro gas chromatograph (GC) with two thermal conductivity detectors, a mass spectrometer (GCMS-QP5000, Shimadzu), and a Fourier Transform Infrared Spectrometer (FTIR, FTS-185, Bio-Rad). External standards were used where available to identify and quantify reaction products. Identification of fluorinated products was achieved through the use of the FTIR cell and subsequent comparison with library database spectra. HBr and HF were sampled periodically by a water-scrubber. HBr acid was quantified by adding 0.01M AgNO_3 solution and then drying and weighing the solid AgBr. Quantitative analysis of HF acid was made by an ion selective electrode. Using these techniques, all major products were determined, although there are a number of minor products yet to be identified.

A series of 5 space velocities (GHSV) at each temperature were performed for a given inlet concentration matrix by altering flow rates of each feed gas. Two runs were repeated to provide replicates.

RESULTS AND DISCUSSION

Activity of CuZSM5

The catalytic ability was interpreted by the conversion levels of both CBrF_3 and CH_4 . Figure 1 shows the conversion behavior of CBrF_3 and CH_4 with time-on-stream for the reaction over CuZSM5 at 873 K, GHSV of 3600h^{-1} and $\text{CBrF}_3 : \text{CH}_4 : \text{N}_2=1 : 1 : 10$ (volume).

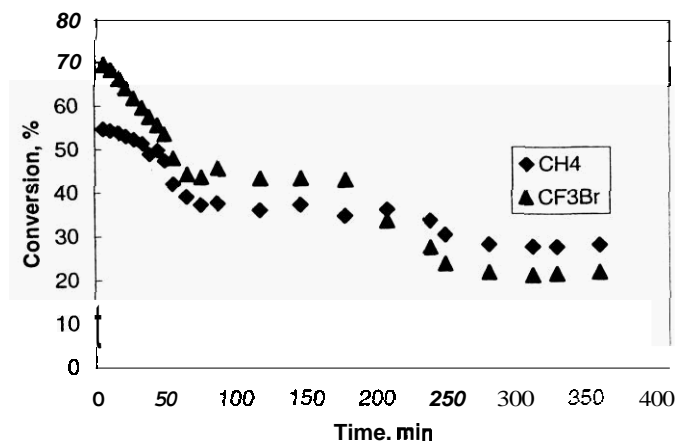


Figure 1. Conversion of CBrF_3 vs time-on-stream over various catalysts at 873 K, GHSV of 3600h⁻¹, and $\text{CBrF}_3 : \text{CH}_4 : \text{N}_2 = 1 : 1 : 10$ (volume).

It was noticed that CuZSM5 had high activity at the initial stage, but deactivated rapidly by around 40% and then had a stable conversion for 120 min. After this period, the catalyst deactivated very fast and achieved another stable state after 300 min. This phenomenon suggests that CuZSM5 deactivated in two steps.

X-ray powder diffraction measurements showed that the catalyst studied in this work remained crystalline ZSM5, indicating the loss of activity was not caused by collapse of the zeolite lattice. However, the agglomeration of some active component Cu^{2+} was detected, and this was believed to be the main cause of the deactivation.

A range of methylated silicone oils were detected, such as $\text{C}_6\text{H}_{18}\text{O}_3\text{Si}_3$, $\text{C}_8\text{H}_{24}\text{O}_4\text{Si}_4$, and $\text{C}_{10}\text{H}_{30}\text{O}_5\text{Si}_5$, but most of them were $\text{C}_6\text{H}_{18}\text{O}_3\text{Si}_3$. It was believed that CH_4 has reacted with CuZSM5 structures, and this was one of the causes of CuZSM5 deactivation.

Coke was formed over CuZSM5, but coke formation probably did not cause much deactivation because the used catalyst did not recover its activity after it was treated by O_2 at 350 °C for 3 hrs. However, more work is needed to identify the reasons of the observed deactivation.

Effects of NiZSM5 on Conversion

For the purpose of comparison, conversion and products distributions after 100 min-on-stream (first stable period) were chosen. Figures 2 and 3 show percentages of CBrF_3 and CH_4 as a function of reaction temperature over CuZSM5 at a fixed GHSV of 3600h⁻¹. It was noticed that conversion levels of both CBrF_3 and CH_4 increased with increasing temperatures and decreased with increasing space velocity (GHSV). At a low conversion level (<15%), the conversion of CBrF_3 was approximately equal to that of CH_4 , and this behaviour was also observed over NiZSM5 [7]. With increasing overall conversion levels, there was less CH_4 consumed than CBrF_3 .

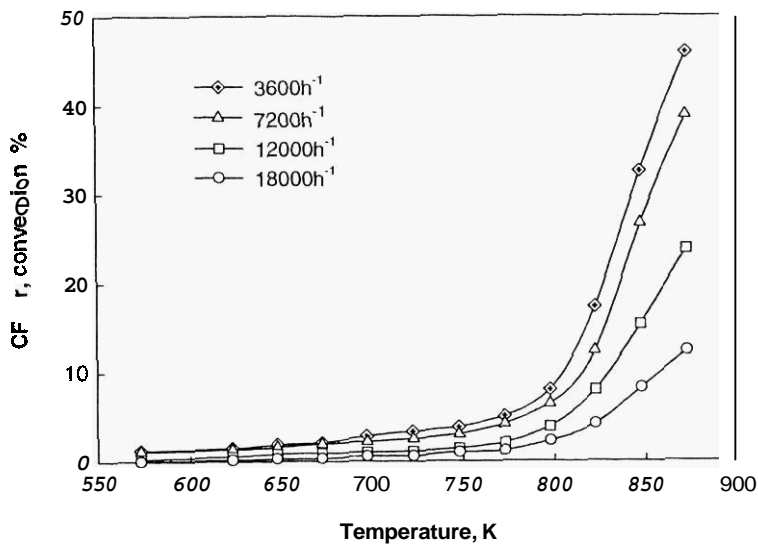


Figure 2. Conversion of CBrF_3 vs temperature at different GHSV. $\text{CBrF}_3 : \text{CH}_4 : \text{N}_2 = 1 : 1 : 10$ (volume).

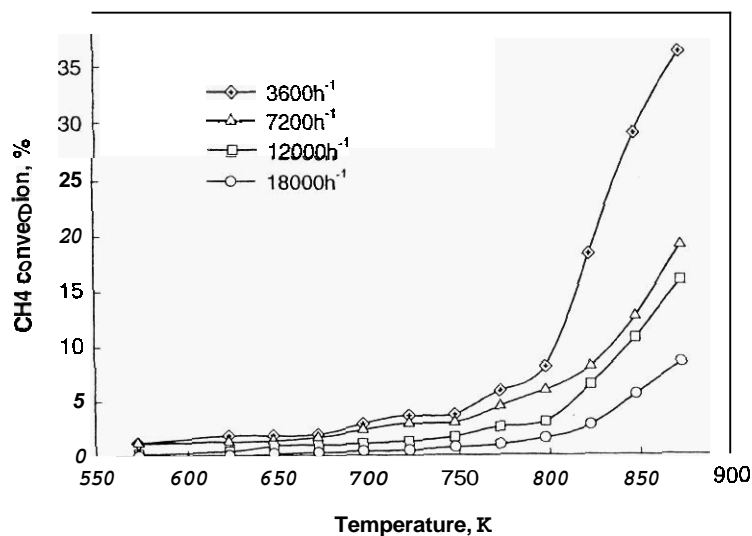


Figure 3. Conversion of CH_4 vs temperature at different GHSV. $\text{CBrF}_3 : \text{CH}_4 : \text{N}_2 = 1 : 1 : 10$ (volume).

Effects of NiZSM5 on Products

The catalytic hydrodehalogenation of Halon 1301 with methane was very complicated and highly selective. Apart from mineral acids HBr and HF, CHF_3 and CH_3Br are the two major products, accounting for more than 90% of all products at temperatures below 823 K (Figure 4). Above 823 K, coke formation increased quickly with increasing temperature.

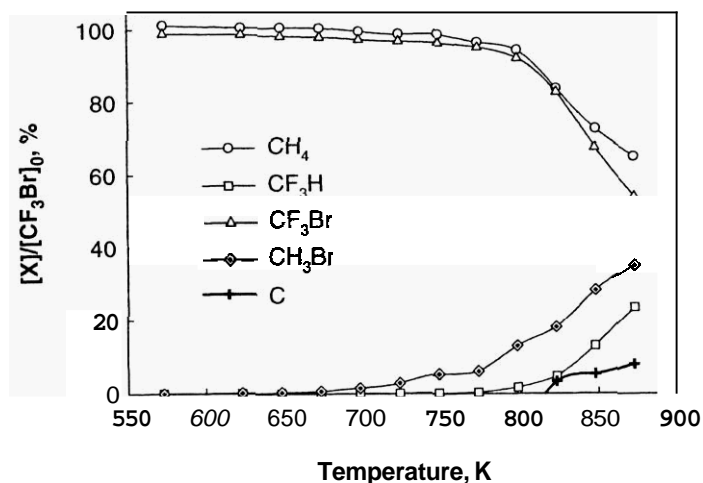


Figure 4. Major products distribution vs temperature at GHSV of 3600h^{-1} . $\text{CBrF}_3 : \text{CH}_4 : \text{N}_2 = 1 : 1 : 10$ (volume).

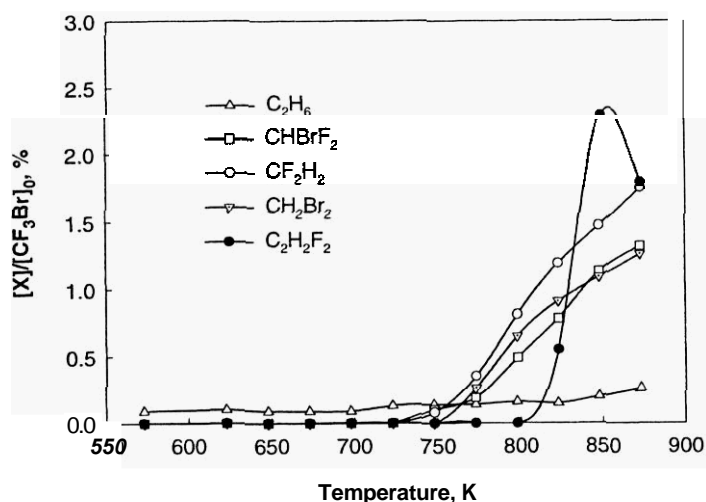


Figure 5. Minor products distribution vs temperature at GHSV of 3600h^{-1} . $\text{CBrF}_3 : \text{CH}_4 : \text{N}_2 = 1 : 1 : 10$ (volume).

A number of minor products are formed, such as C_2H_6 , CH_2Br_2 , CHBrF_2 , CH_2F_2 , $\text{C}_2\text{H}_2\text{F}_2$, CH_2BrF , C_2H_2 , C_2F_4 , and C_2H_4 ; however, Figure 5 only depicts the distribution of five of them, because the rest were in much lower amounts. It was found that the selectivity to C_2H_6 showed only insignificant variations with temperature. The formation of $\text{C}_2\text{H}_2\text{F}_2$ was dependent on the temperature and decreased with raising the temperature above 850 K, suggesting that this species was intermediate. The production of CHBrF_2 , CH_2F_2 , and CH_2Br_2 all increased with increasing temperature, and CH_2F_2 is a good replacement for halons.

CONCLUSION

The hydrodehalogenation of Halon 1301 with methane was investigated over CuZSM5 at ambient atmosphere, over a temperature range from 573 K to 873 K and GHSV from 3600 h⁻¹ to 18000 h⁻¹. CuZSM5 (2.0wt%) showed some catalytic activity during a 360-min test. Its two stable periods implied the complicated mechanism of its catalytic deactivation. The agglomeration of active site Cu²⁺ and the partial methylation of the framework of CuZSM5 were believed to be two causes of deactivation. The conversion levels of both CBrF₃ and CH₄ increased with increasing temperature, and at high temperature, the conversion of CBrF₃ was higher than that of CH₄. Products constituted CHF₃, CH₃Br, C₂H₆, CH₂Br₂, CHBrF₂, CH₂F₂, C₂H₂F₂, CH₂BrF, C₂H₂, C₂F₄, C₂H₄, and coke, but only CHF₃ and CH₃Br were major products. More work is needed to confirm the durability of CuZSM5, and the mechanism of the reaction is yet to be explained.

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