

# Catalytic reaction of methane with CBrF<sub>3</sub>

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The catalytic reaction of CH<sub>4</sub> with CBrF<sub>3</sub> over Co, Cu and Mn ZSM-5 zeolites is described; major products (at low temperatures) are those expected for simple hydrodebromination: CH<sub>3</sub>Br and CHF<sub>3</sub>.

The hydrodehalogenation reaction of chlorofluorocarbons (CFCs) and bromofluorocarbons or bromochlorofluorocarbons (halons) are potentially important reactions for both disposal of ozone depleting chemicals and production of hydrofluorocarbon replacements. Previous work in this area has focussed on reactions of CFCs with hydrogen over supported palladium catalysts.<sup>1–12</sup> Little attention has been paid to the corresponding hydrodebromination of halons. Here we describe for the first time the catalytic reaction of halon 1301 (CBrF<sub>3</sub>) with methane over transition metal exchanged ZSM-5 zeolites. This novel catalytic reaction offers potential new routes to hydrofluorocarbons using methane as the hydrogen source.

Cobalt, copper and manganese exchanged ZSM-5 zeolites were prepared from a commercial ZSM-5 (PQ, Si/Al = 25), and charged into an alumina plug flow microreactor. Reactant gas stream (CH<sub>4</sub>–CBrF<sub>3</sub>–N<sub>2</sub> = 1:1:10) was flowed over the catalyst at a GHSV of 3500 h<sup>–1</sup>, and products were analyzed by on-line gas chromatography after passing through a caustic scrubber.

Fig. 1 shows typical CBrF<sub>3</sub> conversions *versus* time on stream over four different zeolite catalysts at 873 K. Also shown is the corresponding conversion in the homogeneous reaction, as reported elsewhere.<sup>13</sup> The gas phase reaction between CH<sub>4</sub> and CBrF<sub>3</sub> begins at *ca.* 800 K, and increases dramatically above 900 K. A striking feature of the reaction in the presence of zeolite catalysts is the initial high conversion of CBrF<sub>3</sub> which then falls to a steady state value. Our preliminary investigations of this breakthrough period suggest reaction of CBrF<sub>3</sub> with the zeolite which generates the active phase for the hydrodehalogenation reaction. <sup>27</sup>Al MAS NMR measurements show that framework tetrahedral aluminium in the zeolite is completely transformed into an as yet unidentified form, although XRD analysis shows no change in the zeolite structure. In the case of HZSM-5, the steady state conversion approaches that found in the absence of catalyst. For the transition metal

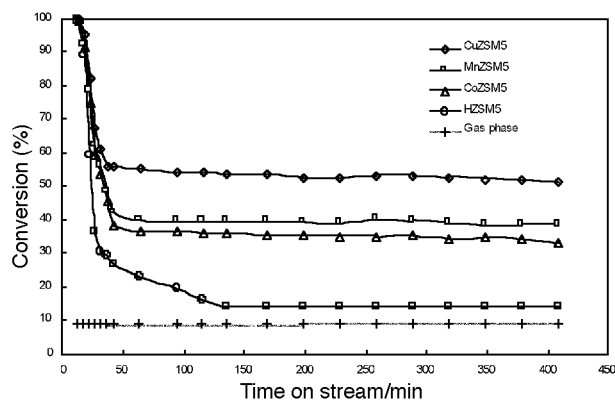


Fig. 1 Conversion of CBrF<sub>3</sub> *versus* time on stream at 873 K over various catalysts.

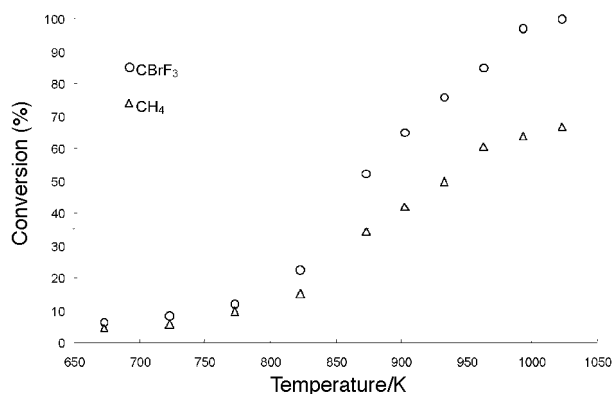


Fig. 2 Steady state conversion of CBrF<sub>3</sub> and CH<sub>4</sub> *versus* temperature over MnZSM-5.

exchanged zeolites, however, there is a very evident influence of catalyst on the steady state conversion. It is important to note that zeolite crystallinity is fully retained during this reaction, even after 36 h on stream.

Fig. 2 plots the steady state CBrF<sub>3</sub> and CH<sub>4</sub> conversions *versus* reaction temperature over MnZSM-5; similar profiles were measured for the other transition metal zeolites. The CBrF<sub>3</sub> conversion exceeds that of CH<sub>4</sub> at all temperatures, suggesting that the reaction pathway is more complex than that predicted for the simple 1:1 stoichiometry of reaction (1):



In separate experiments, we have noted that CBrF<sub>3</sub> undergoes pyrolysis reactions over the same catalysts, producing C<sub>2</sub>F<sub>6</sub> and Br<sub>2</sub>,<sup>14</sup> and C<sub>2</sub>F<sub>6</sub> was detected as a minor product also in the reactions with methane. The major reaction products detected in the reactions with methane at lower temperatures are those expected from reaction (1), as illustrated in Fig. 3. Above 873 K, however, the yield of CH<sub>3</sub>Br declines, and other reaction products appear, (notably hydrocarbons C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>), due to further reaction of CH<sub>3</sub>Br. Other products identified include C<sub>2</sub>H<sub>2</sub>F<sub>2</sub>, C<sub>2</sub>H<sub>3</sub>Br, CH<sub>2</sub>Br<sub>2</sub>, and trace (less than 5 ppm) quantities of C<sub>2</sub>HBrF<sub>2</sub>, C<sub>2</sub>HBr<sub>2</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>2</sub>H<sub>3</sub>F<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>Br and H<sub>2</sub>. Mass balances for all reactions were generally better than ±

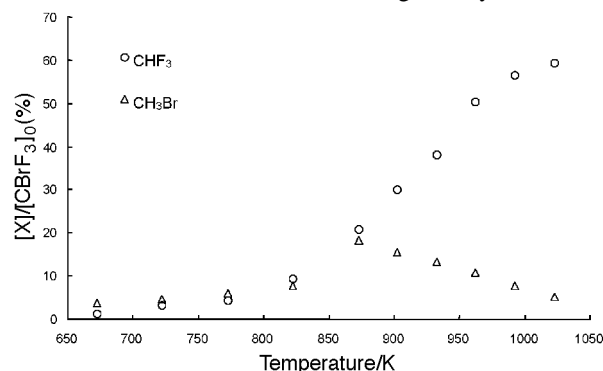


Fig. 3 Steady state conversion of CBrF<sub>3</sub> to major products CHF<sub>3</sub> and CH<sub>3</sub>Br *versus* temperature over MnZSM-5.

3% and usually  $\pm 1\%$ , and suggest any as-yet unidentified species represent only a small fraction of reaction products.

The reaction mechanisms involved in this intriguing chemistry are not yet clear. The high initial conversions of  $\text{CBrF}_3$ , and the results of preliminary characterization experiments on catalysts exposed to  $\text{CBrF}_3$  plus  $\text{CH}_4$  or  $\text{CBrF}_3$  alone for short periods<sup>14</sup> suggest that initial reaction of  $\text{CBrF}_3$  with fresh catalysts generates the catalytically active species. The high reaction selectivity (at low temperatures) may result from the selective cleavage of C–Br bonds in preference to C–F bonds in  $\text{CBrF}_3$ , and reflects the lower relative strength of the C–Br bond ( $295 \text{ kJ mol}^{-1}$ )<sup>15</sup> compared with C–F bonds (*ca.*  $460 \text{ kJ mol}^{-1}$ , estimated from analogous F– $\text{CF}_2\text{Cl}$  bond strength) in  $\text{CF}_3\text{Br}$ . Low temperature cleavage of C–Br would occur before evidence of C–F bond cleavage, leaving the  $\text{CF}_3$  moiety intact.

Further work is needed to optimize catalysts, identify active sites and determine reaction pathways. At present we are also investigating the reactions of CFCs and other halocarbons with methane. The results presented here offer a new route for methane utilization in the disposal and upgrading of ozone depleting materials.

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