Catalytic reaction of methane with $CBrF_3$

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The catalytic reaction of CH_4 with $CBrF_3$ over Co, Cu and Mn ZSM-5 zeolites is described; major products (at low temperatures) are those expected for simple hydrodebromination: CH_3Br and CHF_3.

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.[1–12] Little attention has been paid to the corresponding hydrodebromination of halons. Here we describe for the first time the catalytic reaction of halon 1301 ($CBrF_3$) 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_4–$CBrF_3$–N_2 = 1 : 1 : 10) was flowed over the catalyst at a GHSV of 3500 h^{-1}, and products were analyzed by on-line gas chromatography after passing through a caustic scrubber.

Fig. 1 shows typical $CBrF_3$ 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.[13] The gas phase reaction between CH_4 and $CBrF_3$ 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 $CBrF_3$ which then falls to a steady state value. Our preliminary investigations of this breakthrough period suggest reaction of $CBrF_3$ with the zeolite which generates the active phase for the hydro-dehalogenation reaction. ^{27}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
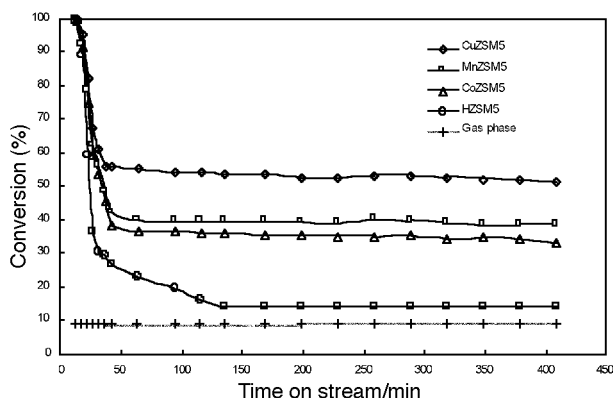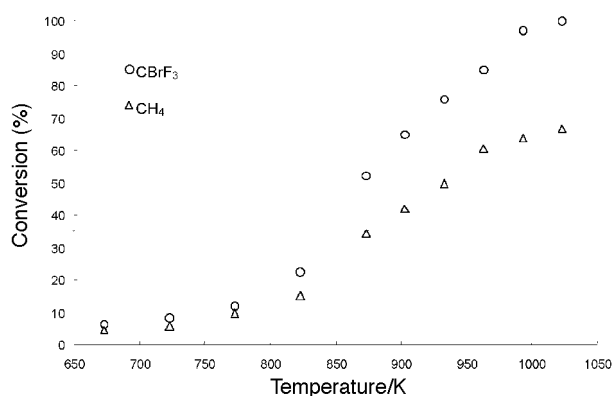

Fig. 2 Steady state conversion of $CBrF_3$ and CH_4 *versus* temperature over MnZSM-5.

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 $CBrF_3$ and CH_4 conversions *versus* reaction temperature over MnZSM-5; similar profiles were measured for the other transition metal zeolites. The $CBrF_3$ conversion exceeds that of CH_4 at all temperatures, suggesting that the reaction pathway is more complex than that predicted for the simple 1:1 stoichiometry of reaction (1):

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

In separate experiments, we have noted that $CBrF_3$ undergoes pyrolysis reactions over the same catalysts, producing C_2F_6 and Br_2,[14] and C_2F_6 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_3Br declines, and other reaction products appear, (notably hydrocarbons C_2H_4 and C_2H_2), due to further reaction of CH_3Br. Other products identified include $C_2H_2F_2$, C_2H_3Br, CH_2BrF, and trace (less than 5 ppm) quantities of $C_2HBr_2F_3$, CH_2Br_2, C_2F_6, $C_2H_3F_3$, C_6H_5Br and H_2. Mass balances for all reactions were generally better than ±

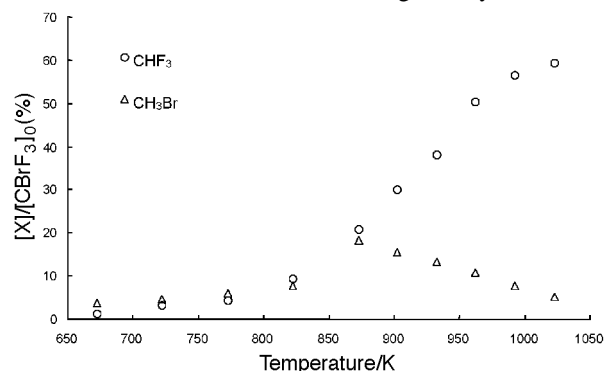**Fig. 1** Conversion of $CBrF_3$ *versus* time on stream at 873 K over various catalysts.

Fig. 3 Steady state conversion of $CBrF_3$ to major products CHF_3 and CH_3Br *versus* temperature over MnZSM-5.

3% and usually ± 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 $CBrF_3$, and the results of preliminary characterization experiments on catalysts exposed to $CBrF_3$ plus CH_4 or $CBrF_3$ alone for short periods[14] suggest that initial reaction of $CBrF_3$ 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 $CBrF_3$, and reflects the lower relative strength of the C–Br bond (295 kJ mol^{-1})[15] compared with C–F bonds (*ca.* 460 kJ mol^{-1}, estimated from analogous F–CF_2Cl bond strength) in CF_3Br. Low temperature cleavage of C–Br would occur before evidence of C–F bond cleavage, leaving the 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.

Notes and references

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