

C₁ Coupling via Bromine Activation and Tandem Catalytic Condensation and Neutralization over CaO/Zeolite Composites.

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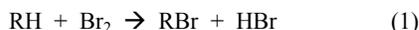
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Introduction

Although much of the world's methane is stranded, utilization of available methane as a chemical feedstock begins in practice with its conversion to methanol by partial oxidation to syn gas followed by recondensation. Subsequent conversion of CH₃OH to olefins was made possible by discoveries in the early seventies by Mobil scientists,¹⁻⁴ and later generalized by other workers to CH₃X (X = halide, SH, NH₂, OCH₃) condensation.⁵⁻¹⁴ The proposed mechanism^{15, 16} is an initial dehydrative coupling to form the actual catalyst, a relatively ill-defined adsorbed cyclic hydrocarbocation (carbon pool). The technology has been widely developed for multiple product outputs, and may be considered an alternative to the reliable but extreme steam cracking method of olefin production from low and middle petroleum distillates. For CH₃Cl, formed from CH₄ oxychlorination, the product in most cases is an aromatic-rich liquid together with HCl and water,⁸⁻⁹ with some variation depending on the promoters used.¹⁰⁻¹⁴ While this chloromethane chemistry has been well characterized and the kinetics are favorable, the process has not been commercialized.

Above, we demonstrated a two step technique for partial oxidation of alkanes by oxygen in which a two electron oxidation of a C-H bond is effected by bromine, giving HBr and bromoalkane (Equation 1).¹⁷⁻²⁰



These intermediates were further converted either to unsaturated hydrocarbons (for C₂+) or to oxygenates by reaction with a metal oxide solid reactant. The metal oxide served to remove HBr actively, and to direct the output to specific partial oxidation products dependent upon the metal oxide composition and reaction conditions. Complete recovery of bromine and regeneration of the metal oxide was accomplished by reaction of the spent solid with O₂.

During the course of development of active and regenerable metathesis materials, oxides of calcium were investigated because of their lack of facile redox activity (leading to deep oxidation), stoichiometric HBr neutralization capacity, and the nearly thermoneutral regeneration of CaBr₂ with O₂ to give CaO and Br₂ ($\Delta G^\circ = 14.9$ kcal/mol). We observed that while activated HZSM-5 (Si:Al = 80) rapidly lost catalytic CH₃Br coupling activity over the course of 10 minutes, calcium oxide zeolite composites[#] quantitatively neutralized HBr and effected the presumably superacidic condensation of methyl bromide to higher olefins (Eq. 2).



Figure 1 shows the time dependent product output from two serial continuous flow reactors for methane bromination (1) at 525° C. followed by reaction over a bed of CaO-ZSM-5 at 400° C. (2). Retention of bromine within the second packed bed under these conditions is better than 99.9%, while the product output is very similar to that observed for CH₃OH coupling over Ca/ZSM-5.²¹

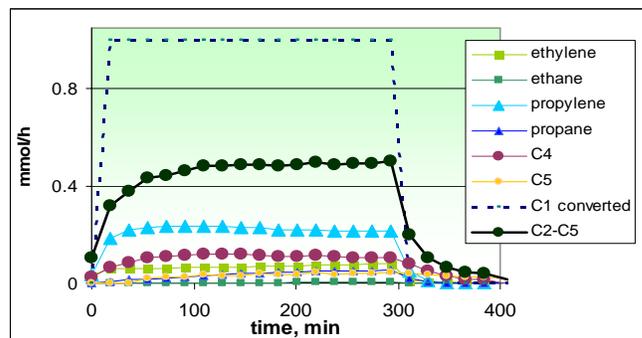
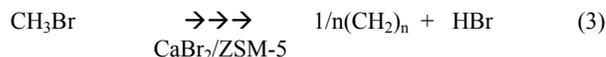


Fig. 1. Output of dual stage reactor with a feed of CH₄:Br₂ (5:0.5 cc/min). First Stage: Plug flow reactor (1 x 100 mm glass tube, 500° C. space time = 0.3 s. Br₂ conversion = 100%, CH₄ conversion = 8.2%). Second Stage: Fixed bed: (10 x 100 mm plug of 5 g. Ca-ZSM-5, 400 C, space time = 20 s, WHSV = 0.04 h⁻¹).

The reaction in Figure 1 represents HBr sequestration to 50-75% of neutralization capacity (5 hours, 5cc/min CH₄, 0.5 cc/min Br₂(g)) of the solid. After more than 10 runs and regenerations (525 C, 5 hours, 5 cc/min O₂, quantitative Br₂ recovery), the coupling/neutralization reactivity and product distribution of the regenerated solid (50% selectivity to C₂-C₅) remained unchanged within experimental error. Furthermore, these materials are also catalytic (Eq. 3) in that even after HBr breakthrough due to metal



oxide depletion, the conversion of bromomethanes under the conditions shown in Figure 1 continues (Figure 2). This catalytic reactivity allows use of more specialized auxiliary metal oxides for HBr sequestration and Br₂ recovery.

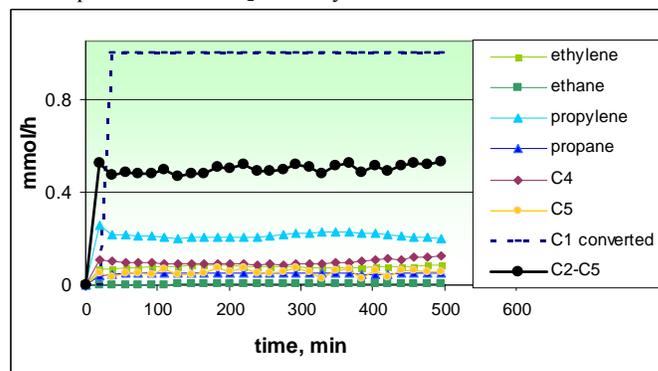


Figure 2. Continued methane bromination and condensation over the same Ca/ZSM-5 bed (5.0 g) used in Figure 1 past the HBr saturation limit (reached at ~100 min) of the bed. Feed: CH₄:Br₂ (5:0.5 cc/min). First Stage: Plug flow reactor (1 x 100 mm glass tube, 500° C. space time = 0.3 s. Br₂ conversion = 100%, CH₄ conversion = 8.2%). Second Stage: Fixed bed: (10 x 100 mm plug of 5 g. Ca-ZSM-5, 400 C, space time = 20 s, WHSV = 0.04 h⁻¹).

Methane partial oxidation by free radical bromination leads to significant buildup of CH_2Br_2 as well as some CHBr_3 at appreciable methane conversion. Over CaO/ZSM-5, CH_2Br_2 condenses predominantly to adsorbed carbon in the absence of CH_3Br while cross coupling between CH_2Br_2 and CH_3Br is manifest in the higher output of aromatics (best represented as mesitylene C_9H_{12}), when both species are present (Figure 3).

Notably, with pure CH_3Br feed, the yield of $\text{C}_2\text{-C}_5$ is significantly higher, and that of adsorbed carbon and aromatics significantly lower than observed for a mixed bromomethane feed, Figure 3.

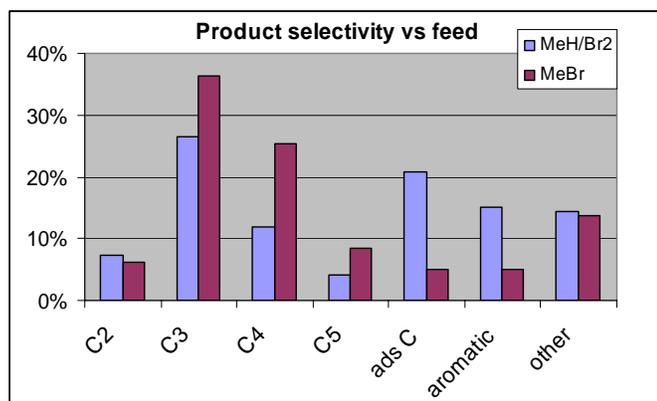


Fig. 3 Comparison of product selectivity for methane/bromine reaction product feed vs pure CH_3Br feed (conditions as in Fig. 1).

The advantage of Br_2 over other halogens in this partial oxidation scheme may be understood in terms of the reduction potential of Br_2 to Br^- (1.07 V vs NHE), which in comparison with Cl_2 (1.36 V) and I_2 (0.54 V), makes alkane bromination significantly less exothermic, yet spontaneous enough to go to completion. Bromine also allows for utilization of a wider range of metal oxides as bromide metathesis reagents because the reoxidation of metal bromides by O_2 (1.23 V) can be accomplished under relatively mild conditions. Despite the slightly lower selectivity for monobromination versus monochlorination for comparable methane conversion, a higher degree of reversibility is expected for the weaker C-Br bonds²² than exists for C-Cl bonds for corresponding C_1 species. In addition, CH_3Br and CH_2Br_2 are expected to be significantly easier to separate from each other than are CH_3Cl and CH_2Cl_2 . Hence polybrominated methanes are not necessarily lost from a methane conversion process and may be induced to compropionate with CH_4 feed, raising overall CH_3Br , and ultimately olefin, yield.²³

We direct further work towards establishing the generality of the condensation reactivity of CH_3Br over microporous solids to give olefins or other products and draw on analogies to CH_3OH coupling.²¹ Ultimately our goal is to utilize the three step low temperature route -- bromination, coupling, regeneration -- to streamline the production of higher hydrocarbons from methane, technology which is presently dominated by processes involving CH_3OH or synthesis gas as intermediates. Selective bromination and reactor configurations favoring compropionate of methane and CH_2Br_2 or CHBr_3 to CH_3Br are potential routes to improved carbon utilization.

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Notes

CaO/ZSM-5 composites were prepared by wet impregnation of 1 part $\text{Ca}(\text{NO}_3)_2$ to 4 parts H-ZSM-5, (Si:Al = 80:1, obtained from Zeolyst Corp.), drying at 125° C. overnight, followed by calcination at 500° C. overnight. Catalytic coupling reactivity was not evident until after the first $\text{CH}_3\text{Br}/\text{HBr}$ metathesis/regeneration cycle.

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