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C_1 Coupling *via* bromine activation and tandem catalytic condensation and neutralization over CaO/zeolite composites†

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We demonstrate here an alternative scheme for C_1 coupling by way of methane bromination, followed by concurrent bromomethane condensation *and* quantitative HBr neutralization; regeneration of the metal oxide with O_2 with recovery of Br_2 completes the cycle.

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 CH_3OH to olefins was made possible by discoveries in the early seventies by Mobil scientists,[1–4] and later generalized by other workers to CH_3X (X = halide, SH, NH_2, OCH_3) 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 CH_3Cl, formed from CH_4 oxychlorination, the product in most cases is an aromatic-rich liquid together with HCl and water,[6,7] with some variation depending on the promoters used.[8–14] While this chloromethane chemistry has been well characterized and the kinetics are favorable, the process has not been commercialized.

We previously reported 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 [eqn. (1)].[17–20]

$$\mathrm{RH} + \mathrm{Br_2} \rightarrow \mathrm{RBr} + \mathrm{HBr} \qquad (1)$$

These intermediates were further converted either to unsaturated hydrocarbons (for C_2+) 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 O_2.

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 $CaBr_2$ with O_2 to give CaO and Br_2 ($\Delta G°$ = 14.9 kcal mol^{-1}). We observed that while activated HZSM-5 (Si : Al = 80) rapidly lost catalytic CH_3Br 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 [eqn. (2)].

$$\mathrm{HBr} + \mathrm{CH_3Br} + \mathrm{CaO/ZSM\text{-}5} \rightarrow 1/n\,(\mathrm{C}_n\mathrm{H}_{2n}) + \mathrm{H_2O} + \mathrm{CaBr_2/ZSM\text{-}5} \qquad (2)$$

Fig. 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 MeOH coupling over Ca/ZSM-5.[21]

The reaction in Fig. 1 represents HBr sequestration to 50–75% of neutralization capacity (5 hours, 5 cm^3 min CH_4, 0.5 cm^3 min $Br_2(g)$) of the solid. After more than 10 runs and regenerations (525 C, 5 hours, 5 cm^3 min O_2, quantitative Br_2 recovery), the coupling/neutralization reactivity and product distribution of the regenerated solid (50% selectivity to C_2–C_5) remained unchanged within experimental error. Furthermore, these materials are also catalytic [eqn. (3)] in that even after HBr breakthrough due to metal oxide depletion, the conversion of bromomethanes under the conditions shown in Fig. 1 continues (Figure S1†). This catalytic reactivity allows use of more specialized auxiliary metal oxides for HBr sequestration and Br_2 recovery.

$$\mathrm{CH_3Br} \xrightarrow[\mathrm{CaBr_2/ZSM\text{-}5}]{} \mathrm{HBr} + 1/n\,(\mathrm{C}_n\mathrm{H}_{2n}) \qquad (3)$$

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 (Fig. 2). Notably, with pure CH_3Br feed, the yield of C_2–C_5 is significantly higher, and that of adsorbed carbon and aromatics significantly lower than observed for a mixed bromomethane feed, Figure S2,† Fig. 2.

The advantage of Br_2 over other halogens in this partial oxidation scheme may be understood in terms of the reduction potential of

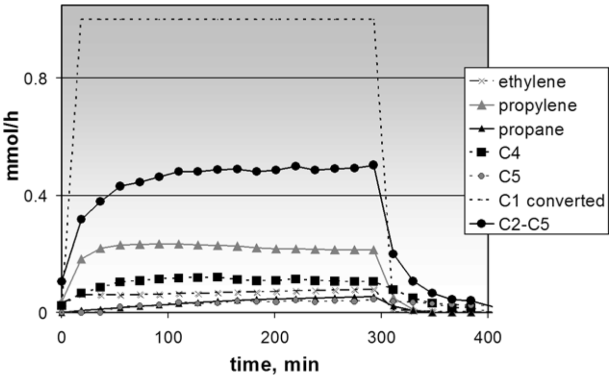

Fig. 1 Output of dual stage reactor with a feed of CH_4 : Br_2 (5 : 0.5 cm^3 min^{-1}). First stage: plug flow reactor (1 × 100 mm glass tube, 500 °C, space time = 0.3 s. Br_2 conversion = 100%, CH_4 conversion = 8.2%). Second stage: fixed bed: (10 × 100 mm plug of 5 g Ca-ZSM-5, 400 C, space time = 20 s, WHSV = 0.04 h^{-1}).

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† Electronic supplementary information (ESI) available: additional figures. See http://www.rsc.org/suppdata/cc/b3/b314118g/

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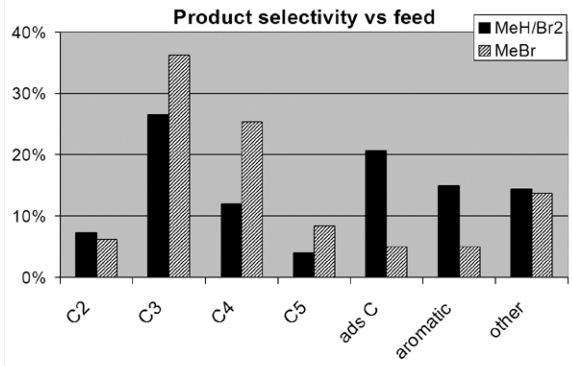

Fig. 2 Comparison of product selectivity for methane/bromine reaction product feed *vs.* pure CH_3Br feed (conditions as in Fig. 1).

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 bonds[22] 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 comproportionate 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 MeOH or synthesis gas as intermediates. Selective bromination and reactor configurations favoring comproportionation of methane and CH_2Br_2 or $CHBr_3$ to CH_3Br are potential routes to improved carbon utilization.

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Notes and references

‡ CaO/ZSM-5 composites were prepared by wet impregnation of 1 part $Ca(NO_3)_2$ 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 CH_3Br/HBr metathesis/regeneration cycle.

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