C_1 oxidative coupling via bromine activation and tandem catalytic condensation and neutralization over CaO/zeolite composites II. Product distribution variation and full bromine confinement

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Abstract

We describe a three-step bromine-mediated process for oxidative coupling of methane using O_2 as oxidant. In the first step, a supported metal bromide solid is treated with O_2 to generate Br_2 and supported metal oxide. The Br_2 thus formed reacts with excess CH_4, giving a mixture of CH_4, bromomethanes, and HBr. This mixture is passed over a CaO/zeolite composite which condenses bromocarbons with 100% conversion to products, and neutralizes HBr to reform the metal bromide. The resulting product contains higher hydrocarbons, excess CH_4, and water. Once the HBr neutralizing capacity of the CaO is spent, the supported $CaBr_2$/ZSM-5 may also serve as catalyst for methyl bromide coupling. The effect of temperature, pressure, and reaction time on the intermediate methane bromination as well as on the overall partial oxidation product distribution is discussed. Incorporation of this scheme into a reactor into which only methane and O_2 are fed is described.
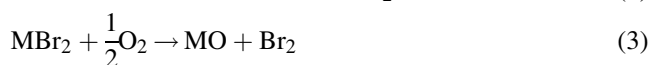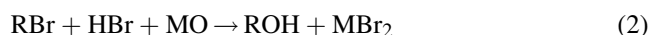© 2004 Elsevier B.V. All rights reserved.

Keywords: Oxidative coupling; Bromine-mediated; Methane activation; Tandem catalytic condensation; CaO/zeolite

1. Introduction

Utilization of available methane as a chemical feedstock begins in practice with its conversion to methanol by partial oxidation to synthesis gas followed by recondensation. Subsequent conversion of CH_3OH to olefins over zeolite catalysts was made possible by discoveries in the early 1970s by Mobil scientists [1–4], and later generalized by other workers to CH_3X (X = halide, SH, NH_2, OCH_3) condensation, also over zeolite catalysts [5–14]. The proposed mechanism for this condensation [15,16] is an initial dehydrative coupling of CH_3X to form the actual catalyst, a distribution of relatively ill-defined adsorbed cyclic hydrocarbocations referred to as the "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 [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.

We recently demonstrated a two-step technique for partial oxidation of alkanes by oxygen ((1)–(4)) [17–20] in which a two-electron oxidation of a C–H bond is effected by Br_2, giving HBr and bromoalkane (1):

$$RH + Br_2 \rightarrow RBr + HBr \tag{1}$$

$$RBr + HBr + MO \rightarrow ROH + MBr_2 \tag{2}$$

$$MBr_2 + \frac{1}{2}O_2 \rightarrow MO + Br_2 \tag{3}$$

$$\text{Sum}: \quad RH + \frac{1}{2}O_2 \rightarrow ROH \tag{4}$$

These bromide intermediates were further converted either to unsaturated hydrocarbons (for C_2^+) or to oxygenates by reaction with a metal oxide solid reactant (2). The metal oxide served to remove HBr, 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 (3).

During the course of development of active and regenerable metathesis materials, we investigated oxides of calcium because of their lack of facile redox activity (which leads to deep oxidation of feed to CO_2), stoichiometric HBr neutralization capacity, and the nearly thermoneutral regeneration of $CaBr_2$ with O_2 to give CaO and Br_2 ($\Delta G^\circ = 14.9$ kcal/mol). We observed that while activated HZSM-5 (Si:Al = 80) rapidly lost catalytic CH_3Br coupling activity over the course of 10 min, calcium oxide zeolite composites effected the presumably superacidic condensation of methyl bromide to higher olefins and quantitatively neutralized HBr (5) [21]:

$$HBr + CH_3Br + CaO/ZSM\text{-}5$$

$$\rightarrow \frac{1}{n}C_nH_{2n} + H_2O + CaBr_2/ZSM\text{-}5 \tag{5}$$
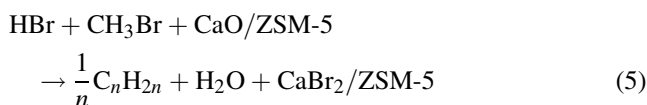
We describe here how the bromomethane coupling product distribution may be controlled by altering temperature and pressure as well as the benefit to the product distribution imparted by maximizing CH_3Br selectivity during bromination. We also describe how the methane bromination product distribution changes with longer space time from a kinetic to an improved, i.e. more selective for CH_3Br, thermodynamic distribution. Finally, we demonstrate that all reactions ((1)–(3)) may be performed in one reactor with a product distribution that is almost identical to that observed starting with bromine as oxidant, and that the concept of the "zone reactor" [22] for methane oxidative coupling, in which the reaction feeds are simply O_2 and CH_4, is viable.

2. Experimental

CaO/ZSM-5 composites were prepared by wet impregnation of one part $Ca(NO_3)_2$ to four parts H-ZSM-5 (Si:Al = 80:1, obtained from Zeolyst Corp.), drying at 125 °C overnight, followed by calcining at 500 °C overnight. Catalytic coupling reactivity was not evident until after the first CH_3Br/HBr metathesis/regeneration cycle. Reactions were performed within Pyrex tubes (either 10 mm and/or 4 mm I.D.) heated in aluminum blocks. Connections between PTFE tubing and to the reactors and bubblers controlling Br_2 influx were made with PTFE tubing and CTFE (valco cheminert) fittings. GC analysis was performed

using an Agilent 6890 gas chromatograph with a 30-m GS-Q capillary column and FID and TCD detection. Methane/ bromine mixtures of variable composition were prepared with bromine entrained in mass flow controlled methane, or methane/N_2 mixtures, using a temperature-controlled bromine bubbler. Experiments demonstrating catalytic bromomethane coupling in which HBr is liberated and no longer neutralized were performed with an aqueous NaOH trap upstream from the gas chromatograph. CH_3Br flow was controlled by cooling a lecture bottle of CH_3Br (b.p. = 4 °C) to temperatures between 10 and 18 °C (below ambient temperature) and attaching a flow restrictor upstream from the reactor, and was calibrated before each run. All other gas flows were controlled using calibrated mass flow controllers. Upon regeneration, bromine and CO_2 output (used to evaluate adsorbed carbon) were quantified using a caustic trap and UV–vis (OBr^- absorbs at 330 nm ($300\ M^{-1}\ cm^{-1}$)), and Sr^{2+} addition for $SrCO_3$ precipitation and gravimetric analysis.

3. Results and discussion

As previously communicated, it was shown that the main products resulting from two serial continuous flow reactors for methane bromination (1) at 400–525 °C, followed by reaction over a bed of CaO–ZSM-5 at 400 °C (Eq. (5)), were ethylene (6% selectivity), propylene (24%), propane (3%), and C_4 (13%). Other products include C_5–C_7 aliphatics (10%), aromatics (toluene, xylenes, mesitylenes, durenes, 15%), and adsorbed carbonaceous material (22%). Subsequent experiments showed that some methane (∼5%) was reformed from intermediate CH_3Br under these conditions. This product distribution is almost identical to that observed for CH_3OH coupling over this same material (data not shown) as well as similar to previously reported CH_3OH coupling over Ca/ZSM-5 [23]. Retention of bromine within the bed of the second reactor under these conditions was better than 99.9%, representing HBr sequestration to 50–75% of neutralization capacity (5 h, 5 cm^3/min CH_4, 0.5 cm^3/min Br_2(g)) of the solid. After more than 50 runs and regenerations (525 °C, 5 h, 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 uncertainty. Furthermore, this material is also catalytic (6) in that even after HBr breakthrough

$$CH_3Br \underset{CaBr_2/ZSM\text{-}5}{\longrightarrow} \frac{1}{n}(CH_2)_n + HBr \tag{6}$$
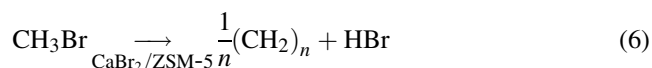
due to metal oxide depletion, the conversion of bromomethanes under the conditions shown described above continues, producing HBr instead of H_2O as a byproduct, without changing the hydrocarbon product distribution (Fig. 1, previously published as a supplemental figure [21] but shown here for purposes of clarity). This catalytic reactivity allows use of more specialized auxiliary metal
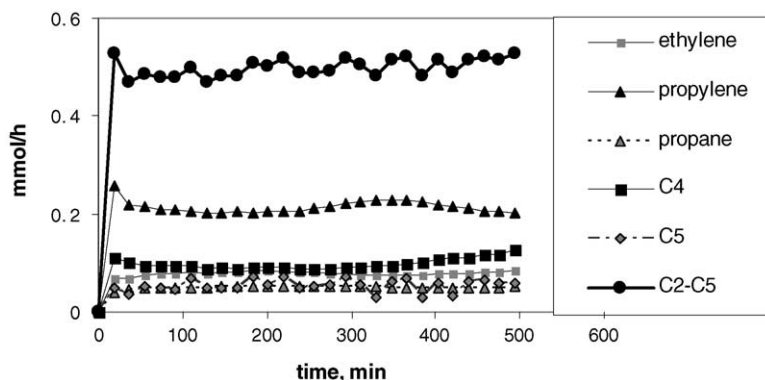
Fig. 1. Methane bromination and condensation over an HBr-saturated bed of Ca/ZSM-5 bed (originally 5.0 g). In this case, the time at which the bed was no longer able to neutralize HBr corresponds to 100 min into this reaction. Feed: CH_4:Br_2 (5:0.5 cm^3/min). First stage: plug flow reactor (1 × 100 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}). The metathesis/coupling bed had been previously run for 300 min at the same feed flow rate as given above, with identical product output. Bromomethanes influx from the methane bromination zone is 1.0 mmol/h. Other products not included in this figure are toluene/xylenes/mesitylenes/durenes (0.15 mmol/h total), carbon (0.25 mmol/h adsorbed), and aliphatic hydrocarbons C6 and higher (0.05 mmol/h) as well as methane reformation (0.05 mmol/h). See Ref. [21] for more details.

oxides for HBr sequestration and Br_2 recovery at still lower temperatures. Importantly, there was no observable affect on the solid of the water product over a range of 0.05–0.5 bar at reaction temperatures.

Methane partial oxidation by free radical bromination leads to significant secondary bromination of CH_3Br leading to 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 [21].

Notably, with pure CH_3Br feed, the yield of C_2–C_7 aliphatics is significantly higher, and that of adsorbed carbon

(4%) and aromatics (5%) significantly lower than observed for a mixed bromomethane feed [21]. The carbon number of the olefin output may be tuned as well. Higher feed pressure (1 bar CH_3Br) and lower temperatures (Fig. 2) favor higher hydrocarbons to the point that significant amounts of hexenes are observable. Because of this favorable coupling product distribution under conditions of low CH_2Br_2 and high CH_3Br, it is important to obtain high selectivity for CH_3Br in the methane bromination step preceding the coupling/neutralization, while maintaining high methane conversion.

Although development of a selective catalyst for methane partial oxidation continues to be a long-term goal, we turned our attention to the relatively mundane effects of
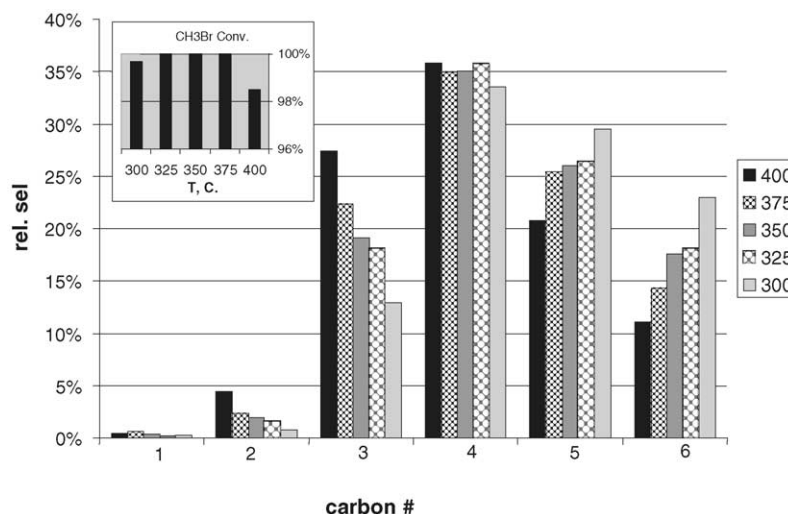

Fig. 2. CH_3Br (13 mmol) coupling products over Ca/ZSM-5 (5 g) as a function of temperature in °C. Conditions: P(CH_3Br) = 1 bar, WHSV = 2 h^{-1}, feed bed residence time ∼3 s. CH_3Br reaction at each temperature was followed by regeneration of the bed with O_2 to recover Br_2. Carbon # = 2 represents ethene, 3 represents propene, 4 represents a mixture of butenes, with trace butanes, 5 and 6 represent all pentenes and pentanes and hexenes and hexanes, respectively. Inset shows methyl bromide conversion.
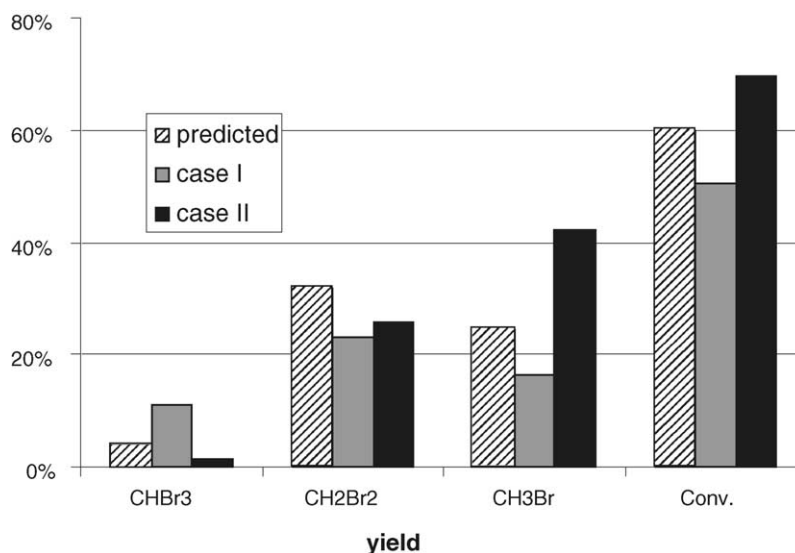
Fig. 3. Methane bromination (CH₄:Br₂ = 1) product distribution under kinetic (500 °C, 1 s space time, "case 1") and thermodynamic conditions (500 °C, 60 s space time, "case 2"). The striped bars represent the predicted thermodynamic distribution using data from the JANAF and TRC databases.

temperature and space time on methane bromination product distribution under conditions of complete bromine conversion to see if any further gain in CH_3Br selectivity was possible. We found that if the methane bromination space time was increased ~60-fold (to ~60 s) over the time necessary for complete bromine consumption, the initial rapidly established product distribution underwent further equilibration that favored higher conversion and higher CH_3Br selectivity (Fig. 3). We rationalize this beneficial effect by considering the kinetics of methane halogenation.

Halogen homolysis may be considered to be the rate-determining step in thermal radical methane halogenations for X = F, Cl, Br. Because halogen–halogen bonds are much weaker than halogen–carbon bonds, reaction of methane with halogen does not necessarily proceed directly to the thermodynamic distribution of hydrohalic acid, halomethanes, and unreacted methane. That is, methane halogenation is typically under kinetic control. The reactions forming methyl and halomethyl radical intermediates from halogen atoms and methane and bromomethane ((7)–(8)) represent the energetic barriers for CH_3X and CH_2X_2 formation, respectively. Because bromomethyl radicals are more stable than corresponding methyl radicals, kinetic control in methane bromination leads to lower selectivity for CH_3Br than thermodynamic control would, if it were achievable, i.e. if C–Br bond formation were reversible. The data in Fig. 3 suggest that we have reached this equilibrated regime:

$$CH_4 + X^\bullet \rightarrow HX + CH_3^\bullet \qquad (7)$$

$$CH_3X + X^\bullet \rightarrow HX + CH_2X^\bullet \qquad (8)$$
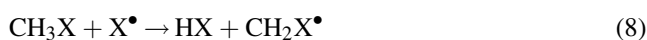
The advantage of Br_2 over other halogens in this partial oxidation scheme may be understood in terms of the reduction potential of Br_2 to Br^- (1.07 V versus NHE),

which in comparison with Cl_2 (1.36 V) and I_2 (0.54 V), renders 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) is, in general, also spontaneous, and can be accomplished under relatively mild conditions. The less positive reduction potential of bromine compared to chlorine is also manifest in C–X bond strengths. Despite the comparable selectivity for monobromination versus monochlorination for comparable methane conversion, a higher degree of reversibility is expected for the weaker C–Br bonds [24,25] than exists for stronger C–Cl bonds for corresponding C_1 species ((9)–(10)), provided that the loss of dibromomethane to coke (11) is not competitive.

$$CH_2X_2 + CH_4 \rightarrow 2CH_3X \qquad (9)$$

r.d.s. for (9) : $\qquad CH_2X_2 \mathfrak{R} CH_2X + X \qquad (10)$

$$CH_2X_2 \rightarrow coke + 2HX \qquad (11)$$

In addition to these energetic arguments, 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 subsequently olefin, yield. While increasing the residence time within the bromination reactor appears to improve the selectivity to CH_3Br, this equilibration zone has now become the bottleneck in the process (regeneration and coupling require 5–10 s for each zone), and therefore this residence time/selectivity tradeoff must be further considered.

Ultimately, it is important to demonstrate that in this scheme oxygen can indeed be used to produce the bromine that was sequestered during a previous metathesis step, and
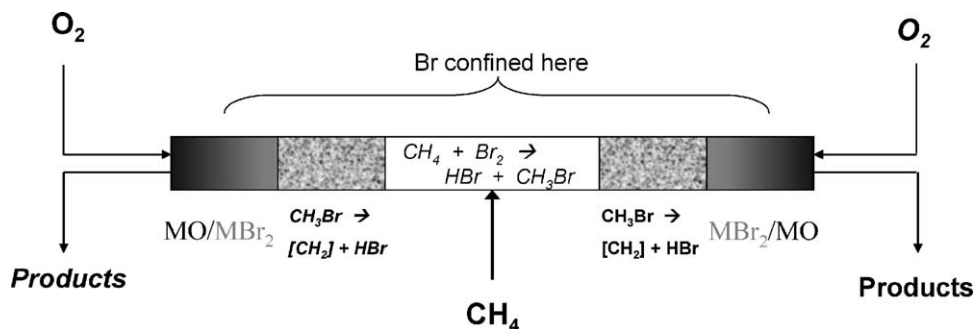
Scheme 1. Zone reactor configuration for bromine-mediated methane partial oxidation. Oxygen enters the reactor at left and reacts with supported metal bromide to release stoichiometric bromine and form supported metal oxide. The Br_2 thus formed passes into the methane bromination reactor where methane feed is introduced and bromomethanes and HBr formed in the ensuing reaction, consuming all Br_2. The bromomethanes and HBr travel into the coupling reactor and react to form higher hydrocarbons and more HBr. All HBr is then neutralized over supported metal oxide to give at the outlet water and higher hydrocarbon products. When the HBr neutralizing metal oxide near the outlet, and the bromine liberating metal bromide at the inlet are depleted, the direction of flow is reversed (feeds shown in italics) and product collected from the other side. At all times bromine/bromide is confined within the reactor.
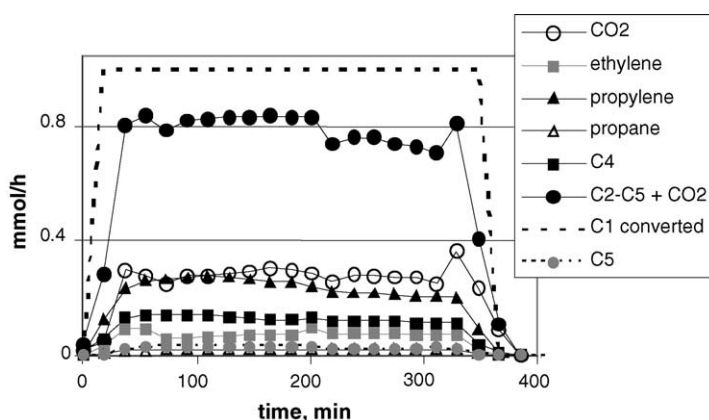

Fig. 4. Reactions products from a reactor into which O_2 is flowed at 0.3 cm^3/min into a metal bromide bed, releasing bromine. The internally formed bromine is then mixed with methane (5 cm^3/min) and reacted at 415 °C to effect methane bromination. The methane bromination products are then passed over a complementary CaO/ZSM-5 bed for coupling and bromine sequestration. The bromine moves through the reactor but never leaves the apparatus. The product distribution is nearly identical to that seen in Fig. 1.

that bromine may be confined within the reactor, allowing operation with alkane and oxygen feed only. Scheme 1 and Fig. 4 describe the result of such an experiment, in which a coupling catalyst/metal bromide bed is treated with oxygen, and releases bromine to react with methane at an intermediate position within the reactor. The intermediates HBr and CH_3Br finally react with the metal oxide as described above, giving bromine-free product. The adsorbed carbon characterized in previous bromination/metathesis runs is in this case also oxidized by O_2 to CO_2. Thus Fig. 4 serves as a proof of the zone reactor concept in a methane partial oxidation scheme.

4. Conclusions

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 [22]. 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 synthesis gas as an intermediate. 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.

Acknowledgement

References

[1] C.D. Chang, A.J. Silvestri, J. Catal. 47 (1977) 249.
[2] C.D. Chang, W.H. Lang, A.J. Silvestri, US Patent 3,998,898 (1976).
[3] C.D. Chang, W.H. Lang, US Patent 3,899,544 (1975).

[4] S.A. Butter, A.T. Jurewicz, W.W. Kaeding, US Patent 3,894,107 (1975).

[5] V.N. Romannikov, K.G. Ione, Kinet. Katal. 25 (1984) 75.

[6] G.A. Olah, H. Doggweiler, J.D. Felberg, S. Frohlich, M.J. Grdina, R. Karpeles, T. Keumi, S.-I. Inaba, W.M. Ip, K. Lammertsma, G. Salem, D.C. Tabor, J. Am. Chem. Soc. 106 (1984) 2143.

[7] R.P. Noceti, C.E. Taylor, US Patent 4,769,504 (1988).

[8] C.E. Taylor, R.P. Noceti, R.R. Schehl, in: D.M. Bibby, C.D. Chang, R.F. Howe, S. Yurchak (Eds.), Methane Conversion, Elsevier, Amsterdam, 1988, p. 483.

[9] C.M. White, L.J. Douglas, J.P. Hackett, R.R. Anderson, Energy Fuels 6 (1992) 76.

[10] Y. Sun, S.M. Campbell, J.H. Lunsford, G.E. Lewis, D. Palke, L.-M. Tau, J. Catal. 143 (1993) 32.

[11] D.K. Murray, T. Howard, P.W. Goguen, T.R. Krawietz, J.F. Haw, J. Am. Chem. Soc. 116 (1994) 6354.

[12] K.-J. Jens, in: D.M. Bibby, C.D. Chang, R.F. Howe, S. Yurchak (Eds.), Methane Conversion, Elsevier, Amsterdam, 1988, p. 491.

[13] J.R. Anderson, Appl. Catal. 47 (1989) 177.

[14] F. Banderman, P. Lersch, Appl. Catal. 75 (1991) 133.

[15] J.F. Haw, W. Song, D.M. Marcus, J.B. Nicholas, Acc. Chem. Res. 36 (2003) 317.

[16] S. Svelle, S. Kolboe, U. Olsbye, O. Swang, J. Phys. Chem. B 107 (2003) 5251.

[17] X.-P. Zhou, A. Yilmaz, G.A. Yilmaz, I.M. Lorkovic, L.E. Laverman, M.J. Weiss, J.H. Sherman, E.W. Mcfarland, G.D. Stucky, P.C. Ford, Chem. Commun. (2003) 2294.

[18] X.-P. Zhou, I.M. Lorkovic, G.D. Stucky, P.C. Ford, J.H. Sherman, P. Grosso, US Patent 6,462,243 (2002).

[19] X.-P. Zhou, I.M. Lorkovic, G.D. Stucky, P.C. Ford, J.H. Sherman, P. Grosso, US Patent 6,472,572 (2002).

[20] X.-P. Zhou, I.M. Lorkovic, J.H. Sherman, US Patent 6,486,368 (2002).

[21] I. Lorkovic, M. Noy, M. Weiss, J. Sherman, G.D. Stucky, P.C. Ford, Chem. Commun. (2004) 566.

[22] P. Grosso, US Patent 6,525,230 (2003).

[23] M. Stoecker, Microporous Mesoporous Mater. 29 (1999) 3.

[24] D.R. Lide, CRC Handbook of Chemistry and Physics 1999–2000: A Ready-Reference Book of Chemical and Physical Data, 81, CRC Press, Boca Raton, FL, 2000.

[25] S.J. Paddison, E. Tschouikow-Roux, J. Phys. Chem. A 102 (1998) 6191.