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Hydrodebromination and Oligomerization of Dibromomethane

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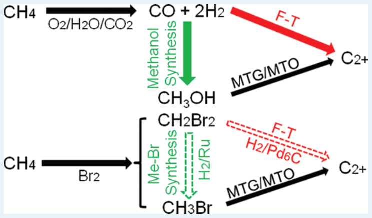
S *Supporting Information*

ABSTRACT: CH_3Br, like CH_3OH in the Methanol-To-Gasoline process, can be readily directly converted to petrochemicals and liquid fuels. CH_3Br can be obtained in high yields by the direct bromination of methane using relatively low reaction temperatures and pressure, but with the formation of dibromomethane (DBM) as a primary side product. Here, we report that DBM can be highly selectively converted to higher hydrocarbons and methyl bromide via a catalytic hydrodebromination process. Silica-supported palladium carbide shows a high selectivity for the conversion of DBM to higher hydrocarbons, mainly light olefins. Silica-supported ruthenium has a high selectivity for the conversion of DBM to methyl bromide, which can then be converted to fuels or light olefins. These reactions offer pathways to increase the overall useful product yield of the methane bromination reaction, thus taking an important step toward the potential industrial application of bromine mediated Gas-To-Liquid technology.



KEYWORDS: *hydrodebromination, oligomerization, gas-to-liquid, methane, Fischer−Tropsch*

■ INTRODUCTION

Methane is an abundant and potentially renewable hydrocarbon resource. Unlike petroleum, which is a liquid and relatively easy to collect remotely and transport, methane is challenging to cost-effectively collect and transport over long distances, and is frequently flared. Conversion of methane gas into a more readily transportable liquid, Gas-To-Liquid (GTL), at the site of collection has long been thought to be the ideal solution.[1−4] Several methods have been developed for the direct conversion of methane,[5] including oxidative coupling,[6,7] aromatization,[8] and selective oxidation into methanol,[9,10] but the yields have not been adequate for commercial deployment. Commercial GTL technology relies on breaking all the C−H bonds in methane in the presence of an oxygen source to produce synthesis gas, CO + H_2, as a transformable intermediate. The synthesis gas can then be used for the Fischer−Tropsch (F-T) synthesis to produce liquid fuels and chemicals. Another route is using synthesis gas for the synthesis of CH_3OH, which is used as a reactant in the Methanol-To-Gasoline process for the synthesis of liquid fuels and chemicals.[2,3] To produce economically competitive products, large commercial facilities are required for GTL conversion processes because of the cost of production (with conversion temperatures usually over 800 °C) of the synthesis-gas intermediate from methane.

A low-temperature, high-yield process with a smaller facility that could be located close to the natural gas sources is highly desirable. From this point of view, the methane halogenation process is promising. The halogen-mediated routes for conversion of methane to higher hydrocarbons are illustrated in Figure 1A. Instead of the high energy-consuming synthesis gas process, methane can be nonselectively converted to halomethanes ($CH_{4-n}X_n$) at relatively low temperatures (below 550 °C).[11−13] Methyl halides such as CH_3Br have been shown to be directly transformed into olefins or higher hydrocarbons by a coupling process analogous to the Methanol-To-Olefins and Methanol-To-Gasoline processes over either zeolites[14−17] or bifunctional acid−base metal oxides.[18] Of the halogens, bromine has the advantage that selectivity for the formation of methyl bromide from the direct reaction of bromine with methane is relatively high; and, the C−Br bond is weak enough to allow for facile bromine removal and recovery for reuse.[11,17] However, the bromination of methane at high conversion also produces significant quantities of dibromomethane (DBM), with small amounts of tribromomethane. In general, the halogenation reaction rate increases in the order: $CH_4 < CH_3X < CH_2X_2 < CHX_3$,[11,12] with polyhalogenation being especially kinetically favored for Cl and F. Because of the reactivity of the polyhalogenated species, catalytic processes for converting these methane halogenation products to end-products have typically resulted in coke formation.[19] Separation of these polyhalomethanes prior to their use in the coupling reactor makes the entire halogen-based GTL process substantially more expensive and less practical.

Several strategies can be applied to solve the polyhalomethane issue. The first is selective halogenations. Olah et al.[11] proposed that since incorporation of halogen atoms into methane makes the carbon progressively more electropositive, the electrophilic reaction with $X^{\delta+}$, which is produced by superelectrophiles, becomes kinetically less favorable. Thereby high methyl halide selectivities could, in principle, be achieved.

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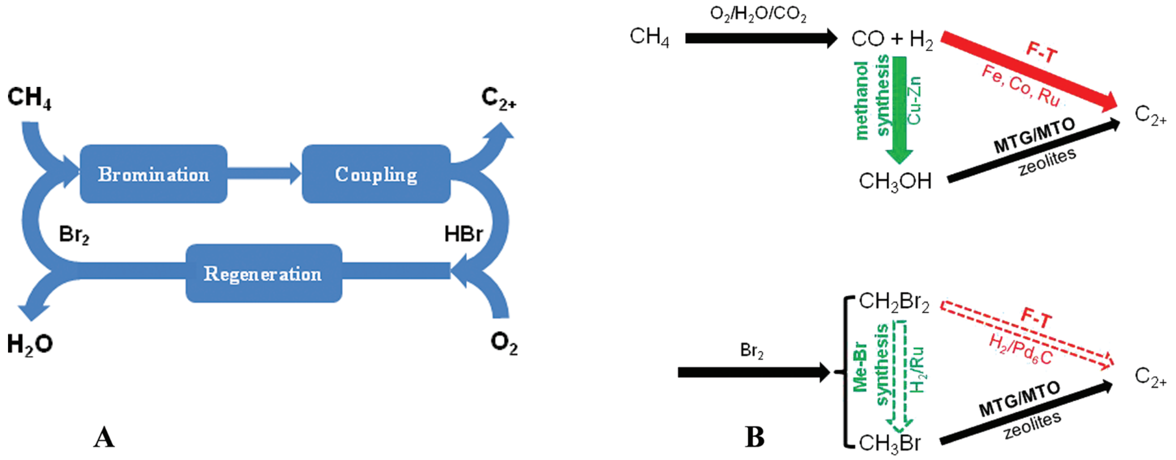


Figure 1. (A) Illustration of halogen mediated methane conversion to higher hydrocarbons; (B) The analogous nature of halogen routes to oxygen routes for methane upgrading. Dashed arrows denote the processes developed in this work.

Following a similar philosophy, Lercher et al.[13] studied methane oxychlorination on LaOCl. Although the underlying rationale is sound, there are no reports of high-yield catalytic selective monohalogenation on catalysts with long-term stability. Another approach is converting the polyhalomethanes into other chemicals with lower coking tendencies, which can be fed into the coupling reactor. Using the polybromomethanes as the halogenating agent for methane has been studied.[12] Although thermodynamically favored, the production of two molecules of methyl bromide from the reaction of DBM and methane requires a relatively long space time. Furthermore, the selectivity for the methyl bromide is limited by thermodynamics. Another approach is to separate the polyhalomethanes from the stream and make use of these compounds to produce value-added chemicals.

Hydrodehalogenation is regarded as the most universal and effective method for the treatment and chemical destruction of organohalide compounds.[20,21] We have been motivated by the catalytic processes used commercially for this important reaction. Group VIII metals are the best known catalysts for hydrodehalogenation because of the ability to dissociate C−X and H−H bonds as well as the high stability.[20−25] In this paper we report our results on the catalytic hydrodebromination and oligomerization of DBM, which is the major byproduct from the reaction of methane and bromine. Among the catalysts studied (Ru/SiO_2, Rh/SiO_2, Pd/SiO_2, Pt/SiO_2, Ag/SiO_2, and Au/SiO_2), palladium carbide formed during the reaction on Pd/SiO_2 showed the highest activity and highest selectivity for coupling products. C_{2+} formation can be regarded as the F-T synthesis analogue. Ru/SiO_2 showed the highest selectivity for methyl bromide, and can be regarded as a methanol synthesis catalyst analogue. Detailed reaction mechanisms are discussed. The analogous nature of halogen and oxygen mediated pathways for the conversion of methane to higher hydrocarbons is illustrated in Figure 1B.

Since propane is a major byproduct in the Methyl Bromide-To-Gasoline process, we intend to make use of propane to provide H_2 for the hydrodebromination process. One possibility is integrating a propane steam reforming unit. Another alternative is adding a propane dehydrogenation unit to provide H_2; meanwhile, more olefin (propylene) will be produced, which is helpful for the Methyl Bromide-To-Gasoline process. Our findings in this paper are directed at solving the DBM issue that hinders the potential industrial application of bromine-mediated GTL technology, and at the same time offering a new route for the synthesis of light olefins.

■ RESULTS AND DISCUSSION

The experimental details and the structure characterizations of the catalysts are given in the Supporting Information, Figures S1 to S3. All the catalysts were prepared into 1 wt % (metal basis) by incipient impregnation, followed by a calcination and activation process before the hydrodebromination reaction. The hydrodebromination reactions were conducted in an atmospheric pressure fixed bed flow reactor system; the configuration of the reaction system was shown in Figure 2.

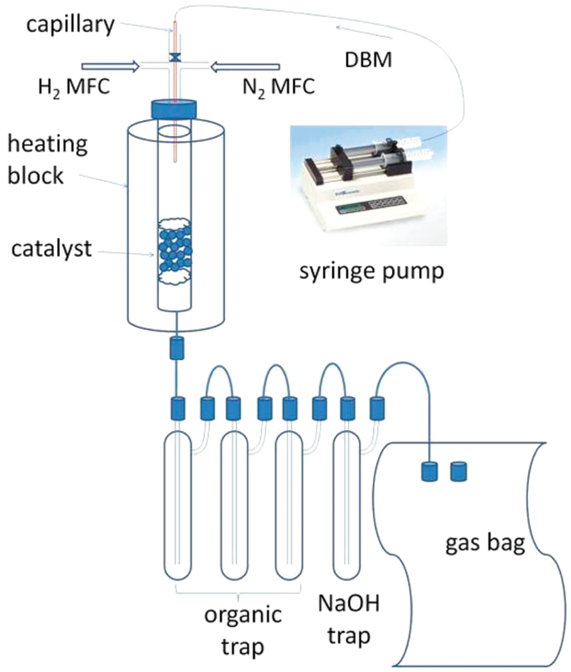


Figure 2. Experimental setup for hydrodebromination reaction: $CH_2Br_2 + H_2 \rightarrow$ products.

After the DBM hydrodebromination reaction was run for 30 min at 350 °C, no significant change was observed in the Ru/SiO_2, Rh/SiO_2, Pt/SiO_2, and Au/SiO_2 structures by X-ray diffraction (XRD) (Supporting Information, Figure S3); however, for the Ag/SiO_2 catalyst, a transformation of the Ag metallic phase into an AgBr phase was observed (Supporting Information, Figure S3). For Pd/SiO_2, all the diffraction peaks

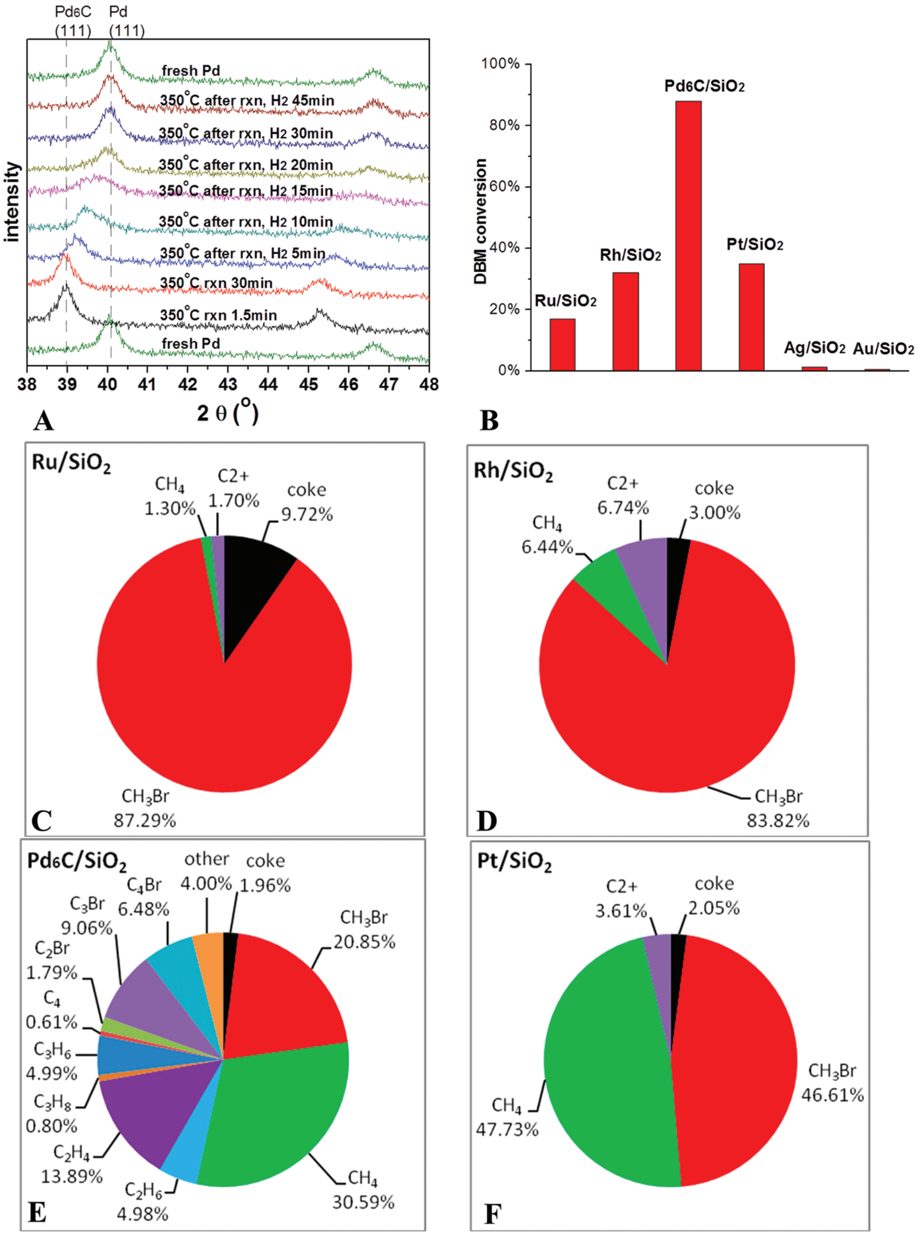


Figure 3. (A) X-ray diffraction patterns of Pd/SiO_2 catalyst after different treatment. The two peaks centered at $2\theta = 39°$ and 40.1° can be assigned to $Pd_6C(111)$ and Pd(111) reflection, respectively; "rxn" denotes DBM hydrodebromination reaction under following condition: 350 °C, $\tau = 2$ s (residence time), DBM:H_2:N_2 mole ratio of 7:14:40; After reaction, the catalysts were treated with H_2:N_2 (14 sccm:40 sccm) at 350 °C for a different period of time. (B) The conversion and (C to F) product distribution of dibromomethane when reacted with hydrogen over different metal catalysts supported on silica: (C) Ru/SiO_2; (D) Rh/SiO_2; (E) Pd_6C/SiO_2, and (F) Pt/SiO_2 (Reaction conditions: 350 °C, $\tau = 2$s, DBM:H_2:N_2 mole ratio of 7:14:40, DBM total input of 8.32 mmol, product distributions are calculated based on carbon moles.).

shifted to lower angles. This behavior can be attributed to the formation of Pd_6C phase, which is very common for Pd catalysts in contact with many hydrocarbons.[26] The Pd-to-Pd_6C phase transformation during hydrodechlorination has been identified by other researchers.[27] After a detailed study of this phase transformation process, we found that the Pd-to-Pd_6C transformation was complete in less than 90 s, while recovery of the metallic Pd in hydrogen, after the DBM was removed, required approximately 30 min, Figure 3A. This indicates that palladium was mainly in the form of Pd_6C during the DBM hydrodebromination reaction instead of metallic Pd.

The conversions of DBM from the reaction with hydrogen at 350 °C on Ru/SiO_2, Rh/SiO_2, Pd_6C/SiO_2, Pt/SiO_2, Ag/SiO_2, and Au/SiO_2 are shown in Figure 3B. The conversions followed approximately the following order: Au/SiO_2, Ag/SiO_2 $\ll$ Ru/SiO_2 < Rh/SiO_2 $\approx$ Pt/SiO_2 < Pd_6C/SiO_2. Since the DBM conversions are determined by many factors, here we are not trying to quantitatively correlate the conversions to the catalytic activities. Ag/SiO_2 and Au/SiO_2 were observed to be relatively inactive for DBM hydrodebromination. These findings are consistent with results reported by other researchers who showed that Ag and Au were inactive for hydrodechlorination reactions.[28,29] The low activity observed for Ag/SiO_2 is explained by the rapid oxidation of Ag to AgBr, which cannot dissociate H_2.[28] Au/SiO_2 was also observed to be relatively inactive and although $AuBr_x$ may not form, dissociation of molecular hydrogen on Au is not facilitated.[29]

We show later in this article that the product distributions from hydrodebromination of DBM over Pd_6C catalyst are

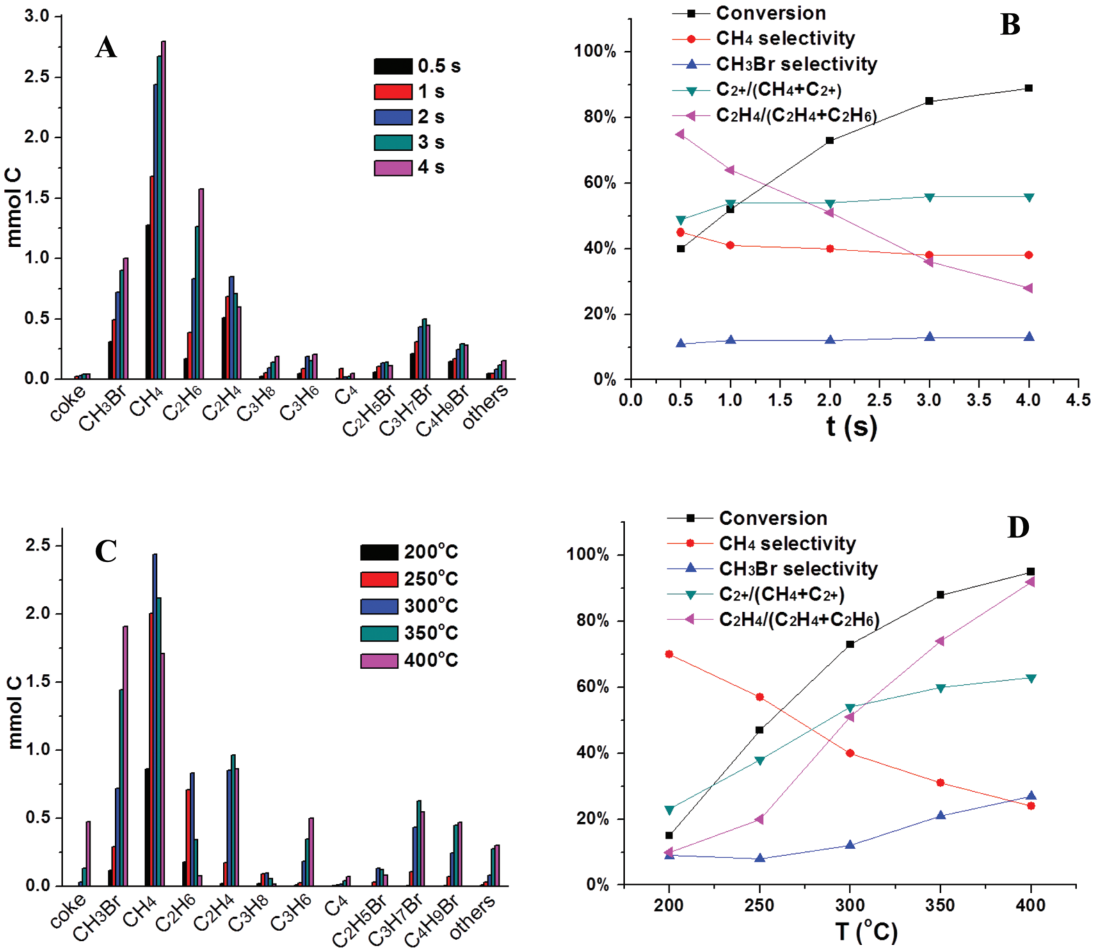


Figure 4. Residence-time-dependent (A and B) and temperature-dependent (C and D) dibromomethane reaction with hydrogen over Pd_6C/SiO_2 catalyst. (A and C) product distribution; (B and D) conversion, CH_4 selectivity, CH_3Br selectivity, $C_{2+}/(CH_4 + C_{2+})$ ratio and $C_2H_4/(C_2H_4 + C_2H_6)$ ratio. All these species were calculated in carbon mole, $C_{2+} = 2n_{C2} + 3n_{C3} + 4n_{C4} + 5n_{C5}$, $n_{Cn} = n_{CnH2n+2} + n_{CnH2n} + n_{CnBr}$ (Reaction conditions: (A and B) 300 °C, DBM:H_2:N_2 mole ratio of 7:14:40, DBM total input of 8.32 mmol; (C and D) τ = 2s, DBM:H_2:N_2 mole ratio of 7:14:40, DBM total input of 8.32 mmol.).

independent of the DBM conversions. Similar behavior also exists for the Ru catalyst. This allows us to compare the product distributions from Pd_6C and Ru with those from Rh and Pt, which possess similar DBM conversions (DBM conversion of 32% and 35% for Rh and Pt). The product distributions from hydrodebromination of DBM over Ru, Rh, Pd_6C, and Pt are shown in Figure 3, C to F. Extremely high methyl bromide selectivity was obtained over Ru, and only trace amounts of methane were observed. For Rh, methyl bromide was still the dominant product (more than 80%); however, methane selectivity increased to approximately 6%. Interestingly, we observed coupling products (C_{2+}) containing up to four carbon atoms. 47% methyl bromide selectivity and 48% methane selectivity were obtained over Pt, while only trace amounts of C_{2+} were observed. DBM hydrodebromination on Pd_6C resulted in production of both methane and coupling products as the major products, while methyl bromide production was greatly suppressed.

Experiments[24] and DFT calculations[30,31] have shown that the halogen and hydrogen adsorption energy on different metal surfaces decreased in the order Ru > Rh > Pt. Stronger adsorption of Br and H on catalyst surfaces makes the HBr desorption process harder and thus leads to higher Br surface coverage. Consequently, the probability for the adsorbed CH_2Br species to desorb without losing another Br, in other words the selectivity toward CH_3Br, will be increased because of the blockage of surface adsorption sites. When we co-fed HBr with DBM-H_2 over Ru and Pt catalysts and kept all the other conditions identical with those shown in Figure 3, B to F, CH_3Br selectivity on Ru increased to 96%, while CH_4, coke, and C_{2+} formation were all suppressed. On Pt, HBr co-feeding led to similar results: CH_3Br selectivity increased to 56%, CH_4 selectivity decreased to 43%, coke and C_{2+} formation were suppressed. A discussion of C_{2+} formation over these catalysts is given later in this paper.

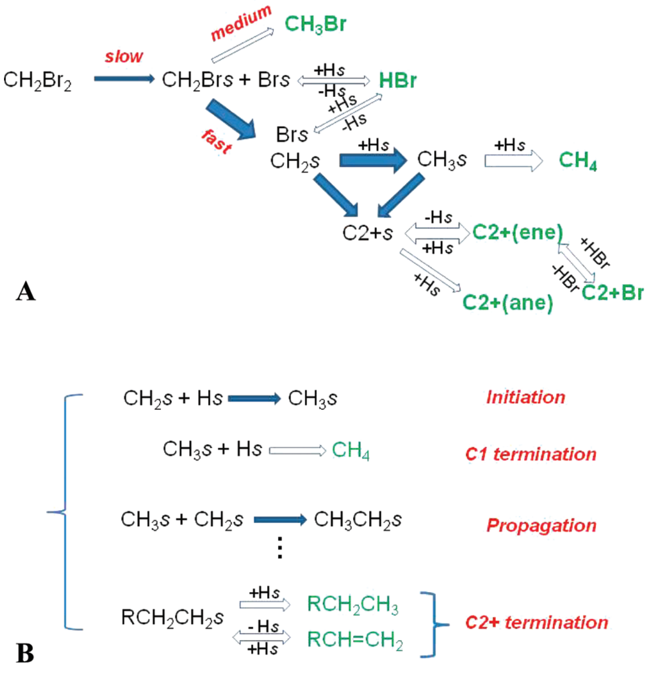
Balancing the price and performance of the Group VIII noble metals, Pd_6C and Ru are promising catalyst candidates for DBM hydrodebromination. Pd_6C showed the highest hydrodebromination activity and C_{2+} products selectivity, while Ru showed the highest CH_3Br selectivity. Preliminary and incomplete optimization led to 60% conversion of DBM on Ru catalyst with a CH_3Br selectivity of above 96%. A time-on-stream reaction was carried out to test the durability of the Pd_6C/SiO_2 catalyst, and the results are shown in Supporting Information, Figure S4. Both conversion and selectivity were unchanged after 5 h on stream.

Detailed studies of DBM hydrodebromination were carried out over Pd_6C/SiO_2 catalyst. The following reaction parameters were studied: residence time, temperature, H_2/DBM ratio, and partial pressure. As shown in Figure 4, A and B, the DBM conversion increased with increasing residence time, while the product distribution stayed the same except that the $C_2H_4/(C_2H_4 + C_2H_6)$ ratio dropped. Compared to C_3 and C_4 olefins, the addition of HBr to ethylene is much slower,[32] which explained the following trend in Figure 4: $C_2Br/C_2 \ll C_3Br/C_3 < C_4Br/C_4$. In a control experiment, we used "NaOH aqueous solution + organic solution" biphase traps instead of the organic traps to collect the products, and the formation of alkyl bromides was greatly suppressed, as shown in Supporting Information, Figure S5. This clearly indicates that most of the alkyl bromides are formed by the addition of HBr to olefins in organic traps. Since C_2Br does not make a significant contribution to the C_2 products distribution, the ratio of $C_2H_4/(C_2H_4 + C_2H_6)$ most likely represent the olefin selectivity of DBM hydrodebromination. Figure 4, C and D show the catalysis results at different temperature. Higher temperature led to higher DBM conversion, higher CH_3Br/CH_4 ratio, higher $C_{2+}/(CH_4 + C_{2+})$ ratio, and also higher olefin selectivity.

Although C_{2+} formation has been reported on dichloromethane (DCM) hydrodechlorination over Pd catalyst,[33,34] the high C_{2+} selectivity (~60%) and olefin selectivity (~90%) achieved in our work has not been reported for DCM. One possible reason is that most DCM hydrodechlorination studies were carried out at relative low temperature (typically below 250 °C) with a high H_2/DBM ratio (typically above 10), which does not favor olefin production. Another contributing factor is the relatively weaker bonds of C−Br and Pd−Br, compared to the C−Cl and Pd−Cl bonds, which may cause higher coverage of carbon species on the palladium surface.

In our proposed DBM hydrodebromination mechanism, which is illustrated in Scheme 1A, the first step would be DBM and H_2 adsorption and dissociation into CH_2Br*s*, Br*s* and H*s* ("*s*" denotes surface). The reverse process, CH_2Br*s* and Br*s* association, is negligible because it is thermodynamically unfavorable. Therefore, the only way for Br*s* to leave the surface is to combine with H*s* and desorb as HBr. This reaction is reversible. The CH_2Br*s* species can go through two parallel processes: combine with H*s* and desorb as CH_3Br; lose the second Br and generate surface carbene species, CH_2*s*. The readsorption of CH_3Br might undergo hydrodebromination to generate CH_4, but this process is slow because the C−Br bond in CH_3Br is stronger than that in CH_2Br_2. Similar conclusions were reached in the hydrodechlorination study of CH_3Cl and CH_2Cl_2.[33,35]

Scheme 1. (A) Potential Pathway for Dibromomethane Reaction with Hydrogen, and (B) Evolution of Surface Carbene over Pd_6C catalyst[a]



[a] Solid arrows indicates adsorption process or surface reaction, hollow arrows indicates desorption process or gas phase reaction. "*s*" denotes surface.

The following trend could be found in the distribution of the DBM hydrodebromination products via a carbene intermediate: $n_{C1} > n_{C2} > n_{C3} > n_{C4}$, which implies that the formation of higher hydrocarbons might follow a F-T mechanism. This is also suggested by the olefin/paraffin ratio at different residence times. The domination of olefins at the short residence time is always regarded as one of the characteristics of F-T synthesis. Ponec et al.[36] first pointed out the analogous nature of the mechanism of hydrodechlorination of polychloromethane to F-T chemistry. This is consistent with Brady and Pettit's work using diazomethane to confirm the carbene mechanism of F-T synthesis.[37] It is generally assumed that there is not just a single reaction pathway on the catalyst surface during the F-T synthesis, but that a number of parallel operating pathways exist. Numerous reaction pathways have been proposed to explain the observed product distribution in the F-T synthesis.[4] However, the carbene mechanism is still the most widely accepted mechanism describing the formation of hydrocarbons. Recent work on the F-T mechanism study using density functional theory (DFT) calculations shows that the carbene mechanism is more favorable than CO-insertion and the hydroxyl-carbene mechanism in many circumstances.[38]

According to Scheme 1B, the surface carbon species evolve to form longer chains via the addition of more and more CH_2*s*. There are two routes for chain termination: combining H*s* and desorbing as paraffins (+H termination), or losing H*s* by β−H elimination and desorbing as olefins (-H termination). Olefins could either readsorb on the catalyst surface and be hydrogenated into paraffins, or react with HBr to generate $C_{2+}Br$ products.

According to the Anderson−Schulz−Flory (ASF) theory,[39] the distribution of the F-T products obeys following equation:

$$f(n) = A \times \alpha^{n-1}$$

$$\ln(f(n)) = n \times \ln \alpha + C$$

Here, $f(n)$ is the number of moles of C_n product, and α is the chain propagation probability. This is defined by

$$\alpha = \frac{R_p}{R_p + R_t}$$

where R_p and R_t are the rates of propagation and termination. If we plot $\ln(f(n))$ as a function of n, the slope of the line will be $\ln \alpha$.

For the products of Pd_6C-catalyzed DBM hydrodebromination, we denote by C_2 the number of moles of the molecules containing two C atoms, that is, $C_2H_4 + C_2H_6 + C_2H_5Br$; C_3 and C_4 are defined in the same way. We do not include CH_3Br in C_1, because CH_3Br is not formed by a carbene route. Except in the case of high temperature (400 °C), all others give linear ASF plots. A representative example is shown in Figure 5A. The α values calculated from these curves are plotted against different reaction parameters (Figure 5, B to E). The α values

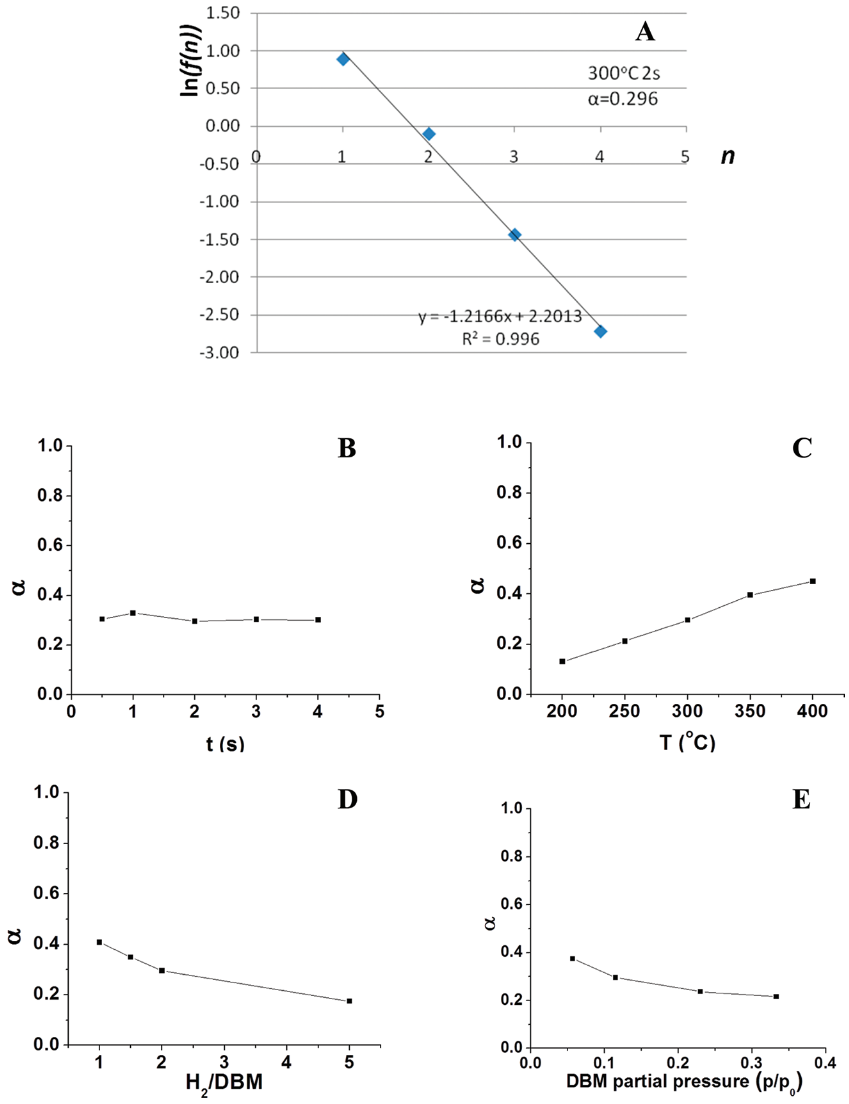


Figure 5. (A) Anderson−Schulz−Flory plotting of the product distribution of dibromomethane reaction with hydrogen over Pd_6C catalyst (300 °C, τ = 2s, DBM:H_2:N_2 mole ratio of 7:14:40, DBM total input of 8.32 mmol). (B to E) Plotting of α values against different reaction parameters (B) residence time (300 °C, DBM:H_2:N_2 mole ratio of 7:14:40, DBM total input of 8.32 mmol); (C) temperature (τ = 2s, DBM:H_2:N_2 mole ratio of 7:14:40, DBM total input of 8.32 mmol); (D) H_2:DBM ratio (300 °C, τ = 2s, DBM total input of 8.32 mmol); (E) DBM partial pressure (300 °C, τ = 2s, DBM:H_2 mole ratio of 1:2, DBM total input of 8.32 mmol).

change little with residence time, increase with temperature, decrease with the H_2/DBM ratio, and decrease with the DBM (H_2) partial pressure (keeping H_2/DBM at a constant ratio).

The change of α with the H_2/DBM ratio is similar to that seen in F-T synthesis, since increasing the ratio of H_2/DBM leads to increased chain termination probability. In DBM hydrodebromination, the change of α value against temperature and partial pressure is opposite to that observed in F-T synthesis.

It is well-known that CO chemisorption is much stronger than H_2 chemisorption, and consequently the catalyst surface was believed to be dominated by carbon species rather than hydrogen under F-T operating conditions.[4] The situation should be reversed in DBM hydrodebromination, because DBM adsorption is a dissociative adsorption, which involves C−Br bond breakage and is much weaker than CO chemisorption. Higher temperatures would favor the dissociative adsorption of DBM, and therefore the surface coverage ratio of carbon species to hydrogen species would be increased and the chain propagation probability (i.e., α) would be increased.

In F-T microkinetics, the reason for α values increasing with system pressure is that the surface concentration of carbon species increase with CO partial pressure, thus increasing the chain propagation probability. For DBM hydrodebromination, the DBM conversion is constant with changing DBM (H_2) partial pressure (keeping H_2/DBM at a constant ratio), which implies that the number of available DBM dissociative adsorption site does not change; so that the carbon species coverage does not change. On the other hand, olefin selectivity decreased with DBM (H_2) partial pressure (Supporting Information, Figure S6), which implies that the surface hydrogen coverage is increased. Consequently, increasing DBM (H_2) partial pressure causes +H chain termination instead of the chain growth probability to be increased, and thereby, the α value is decreased.

To further support the DBM hydrodebromination mechanism, CH_2Br_2 and D_2 were co-fed through Pd/SiO_2 at 300 °C. The product distribution is listed in the Supporting Information, Figure S7. The outlet gas contained 27% DBM and nearly 100% of it was CH_2Br_2: no deuterium-substituted DBM was detected. This is evidence that the C−Br bond scission is irreversible on Pd_6C surface. For the hydrodebromination products, only 2% of methyl bromide contained more than one deuterium atom, while 11% of methane contained more than two deuterium atoms. In a control experiment, a $CH_4 + D_2$ mixture was passed over the same catalyst under the similar reaction conditions and less than 1% of methane was deuterated. This suggests that most of the H/D exchange process took place after DBM molecules were dissociatively adsorbed. The higher degree of H/D exchange for methane compared to methyl bromide indicates that it takes longer for CH_2Br*s* to evolve into CH_2D_2 than into CH_2DBr. This is reasonable since CH_2Br*s* needs to break one C−Br bond and pick up two D*s* to generate CH_2D_2, while it only needs to pick up one D*s* to form CH_2DBr.

The degree of H/D exchange was very high in the longer-chain halocarbons, such as ethyl bromide and propyl bromide. There are three possible explanations for this. First, the longer the carbon chain, the longer it stays on the surface, and the more chance for the H to be exchanged by D. Second, olefins traveling through the catalyst bed are adsorbed and desorbed repeatedly and have a chance to be deuterium-exchanged. The third reason is the "addition-elimination" equilibrium between olefins + HBr/DBr and alkyl bromides.

We compare next the four Group VIII metals studied in this work. It is well-known that the carbon chain growth probability in $CO + H_2$ system under identical conditions satisfies Ru > Rh > Pd > Pt,[40] because the CO bond dissociation ability on the metal surface varies in that order. Brady and Pettit[37] showed that diazomethane + H_2 could reacts on a series of metals, including Ru and Pd, to produce CH_4 and C_{2+}. C_{2+} selectivity is much higher on Ru than on Pd. The most important difference between CH_2N_2 and CH_2Br_2 is that Br is harder to remove from the surface than N_2. Moreover a high Br coverage on Ru and Rh inhibits the dissociation of the second C−Br bond in DBM to generate surface carbenes and blocks the chain growth process. The former effect leads to high CH_3Br selectivity, while the blockage of the chain growth process leads to high selectivity toward CH_4 as opposed to C_{2+}.

For Pt, the surface coverage of Br is low. A considerable amount of surface carbenes are generated, as suggested by the high CH_4 selectivity. However, C_{2+} selectivity is still very low, which indicates that the chain growth probability on Pt surface is quite low. This might be caused by the much higher diffusion rate for H versus CH_x on the Pt surface than on the Pd surface. This idea is supported by the diffusion energy barriers calculated by DFT.[41−44]

Although none of these noble metals has a stable carbide phase under our reaction temperature, a metastable PdC_x phase can be formed under a carbon rich atmosphere,[26] such as C_2H_2, C_2H_4, and CO, as well as DBM, as shown in this work. The formation of a metastable palladium carbide phase will greatly suppress the amount of bulk-dissolved hydrogen, which is believed to be responsible for the nonselective/total hydrogenation of alkynes into alkanes.[45,46] Here the inhibition on hydrogenation behavior by a carbide phase will have a positive effect on C_{2+} formation.

■ CONCLUSIONS

We provide here two potential routes to solve the DBM issue that hinders the industrial application of bromine-mediated GTL technology. In particular, these findings offer a new route for the synthesis of light olefins from methane. The reaction of DBM and hydrogen was studied on several silica supported transition metals. Pd_6C supported on SiO_2 showed the highest selectivity for the conversion of DBM to higher hydrocarbons, mainly light olefins, analogous to the F-T catalysts. Silica-supported ruthenium shows the highest selectivity for the conversion of DBM to methyl bromide, analogous to the methanol synthesis catalysts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and Figures S1−S7. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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