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One-Pot Conversion of Methane to Light Olefins or Higher Hydrocarbons through H-SAPO-34-Catalyzed in Situ Halogenation

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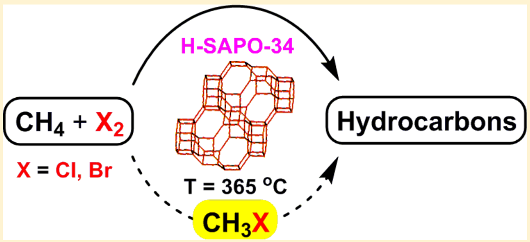
Supporting Information

ABSTRACT: Methane was converted to light olefins (ethene and propene) or higher hydrocarbons in a continuous flow reactor below 375 °C over H-SAPO-34 catalyst via an in situ halogenation (chlorination/bromination) protocol. The reaction conditions can be efficiently tuned toward selective monohalogenation of methane to methyl halides or their in situ oligomerization to higher hydrocarbons. The presence of C5+ hydrocarbons in the reaction products clearly indicates that by using a properly engineered catalyst under optimized reaction conditions, hydrocarbons in the gasoline range can be produced. This approach has significant potential for feasible application in natural gas refining to gasoline and materials under moderate operational conditions.



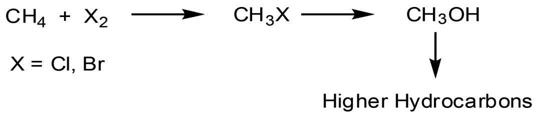
INTRODUCTION

The reserves of natural gas are expected to grow significantly through 2040 with the advances in exploration techniques, horizontal drilling, and hydraulic fracturing technologies coupled with processes for reducing flaring and venting of the gases associated with petroleum.[1] Therefore, methane, the most abundant component of natural gas, may soon become the main raw material. Today, methane is mostly burned to produce energy. Another major industrial application of methane is the high-temperature and cost-intensive steam reforming to produce synthesis gas (CO and H_2), which can be converted to methanol and higher hydrocarbons.[2a−d] The direct heterogeneous conversion of methane to useful chemicals and fuels, generally achieved at temperatures above 500 °C, has so far resulted in limited yields due to severe kinetic limitations.[2e,3] Therefore, an economic large-scale direct functionalization of methane to useful chemicals still remains a big challenge to researchers because of the high stability of methane and the higher reactivity of the desired products.

In liquid superacids, the conversion of methane to higher hydrocarbons was achieved at low temperatures albeit in low yields.[4a] In 1985, Olah et al.[4a,b] proposed a three-step approach for converting methane to hydrocarbons, which involved selective halogenation (chlorination or bromination) of methane to methyl halide with chlorine or bromine as oxidant followed by its hydrolysis to methanol. Its subsequent transformation led to higher hydrocarbons (Scheme 1).

Later, Noceti et al.[4c,d] and others[4e,f,5] presented a two-step process consisting of the oxidative chlorination of methane on Cu-based or rare-earth metal based catalysts followed by the condensation of the methyl chloride to hydrocarbons over a silicoaluminate zeolite (Scheme 2).

Scheme 1. Three-Step Conversion of Methane to Hydrocarbons



Scheme 2. Two-Step Conversion of Methane to Hydrocarbons

$$CH_4 + HCl + O_2 \longrightarrow \text{Chloromethanes} \longrightarrow \text{Hydrocarbons}$$

A two-step approach was developed by Lorkovic et al.[6] to convert methane to methyl bromide/methylene bromide at high temperature followed by condensation to oxygenates and higher hydrocarbons over a solid basic oxide as a catalyst and a source of oxygen. Recently, $EuOBr/ZrO_2$ was shown to be an effective catalyst for the oxybromination of methane to CH_3Br and CH_2Br_2 at 500 °C and is exceptionally stable for the oxidation of HBr to Br_2.[7] Osterwalder and Stark[8] also described a two-step process in which methane could be selectively converted to methyl bromide that was subsequently oligomerized to higher hydrocarbons in a pressurized reactor using $AlBr_3$ as a catalyst at temperatures between 160 and 400 °C. The regeneration of the catalyst and the hydrogenation of the carbonaceous deposits formed during the reaction required a significant amount of hydrogen. Under superacidic $HBr/AlBr_3$ conditions, methane was converted to higher hydrocarbons in a continuous flow reactor at atmospheric pressure between 200 and 400 °C.[9] Under these conditions, $AlBr_3$, a highly corrossive

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and environmentally unsustainable solid Lewis superacid, poses many practical difficulties in the downstream for its separation from the liquid hydrocabon products and make its recyling tedious. Therefore, large-scale conversion of methane to higher hydrocarbons under these conditions is not feasible. The direct conversion of methane at low pressure (10−50 Torr) via a microwave plasma process[10] was shown to produce C2 hydrocarbons. Oxidative coupling of methane to produce ethene and ethane requires high temperatures, generally 500−1000 °C which affects the yields and the stability of the catalyst significantly.[3e,j,k] Ethene undergoes subsequent oligomerization to produce higher hydrocarbons. Recently, nonoxidative reaction of methane above 1000 °C yielded selectively ethene and aromatics.[3j,k] High yields of methyl esters can be obtained under batch conditions using concentrated sulfuric acid or trifluoroacetic acid that need careful hydrolysis to produce methanol and require catalyst regeneration.[11] Therefore, direct conversion of methane to higher hydrocarbons under flow and moderate reaction conditions, i.e., below 400 °C and ambient pressure remains a challenge and a long sought goal.

In our continuing effort to achieve selective monohalogenation of methane, H-SAPO-34, a silicoaluminophospahte zeolite that is isostructural of the chabazite framework topology with a cavity window diameter of 3.8 Å × 3.8 Å and a cavity diameter of 7.3 Å × 12 Å, was used as a catalyst searching for appropriate reaction conditions. It is an excellent catalyst for the methanol-to-olefin and methyl halide-to-olefin processes and quite stable in the presence of HCl or HBr unlike silicoaluminate zeolite. Both chlorination and bromination of methane were conducted at a relatively high dilution level (methane to bromine molar ratio of 10, where deactivation due to carbon deposits is low) and moderate temperatures, safe enough to produce selectively the methyl halide or to expect its conversion directly to higher hydrocarbons.

■ RESULTS AND DISCUSSION

The thermal chlorination is a well-known radical process yielding all chloromethanes as the "reproportionation" reaction with chloroform does not proceed at significant levels at 550 °C while dichloromethane remains inert.[12] In our present work, the thermal chlorination of methane went to completion at 350 °C. The product distribution was almost constant and limited to methyl chloride (87%) and methylene chloride (13%) after 24 h on-stream. The extent of the chlorination was limited to the two first derivatives by the relatively high methane to chlorine ratio employed under a relatively short contact time (about 2.6 s). Initially, in the presence of the catalyst, the conversion of chlorine decreased from 92.3% after 1 h on-stream to 71.5% after 22 h on-stream. The selectivity also dropped from 96.5% methyl chloride to 91.2% during the same period of time, which is probably due to some coke formation. However, after the regeneration of the catalyst at 550 °C with oxygen, the initial conversion was almost restored and the selectivity of methyl chloride was steady at 94.1% after the first 4 h on-stream. The Brønsted acid sites (bridging OH groups) and the acid sites (formed by the reversible interaction of HCl on the Al−O−P groups yielding Al−Cl and P−OH) in the catalyst are capable of polarizing the chlorine molecules to effect the electrophilic chlorination of methane as suggested by Olah et al.[4a,b,13,14]

The conversion of chlorine was found to be lower in the presence of moisture than that observed in the absence of moisture despite the increase of the catalyst loading. However, as the reaction continued, it was found to remain constant (as noticed during the 27 h on-stream, see Figure 1). The selectivity to methyl chloride was remarkably improved (above 98%) and also remained constant. Water seemed to considerably suppress the formation of coke by probably poisoning strong active sites. No carbon oxides were detected in the products.

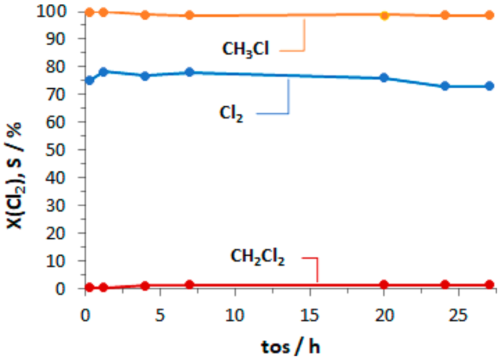


Figure 1. Chlorination over 5 g of H-SAPO-34 at 350 °C with time on-stream in the presence of moisture. $CH_4/Cl_2/N_2/H_2O$ = 10:1:1.3:0.3. Total flow: 600 mL/h·g.

By decreasing the space velocity from 600 (5 g of catalyst) to 420 mL/h·g (7 g), the contact time was increased from approximately 40 to 60 s. At 40 s, the only products observed were methyl chloride (98.7%) and a small amount of methylene chloride (1.3%), though the catalyst turned slightly gray after the reaction.

With a contact time of 60 s, 2 h on-stream, methyl chloride was observed as the sole product (Table 1). However, remarkably, with longer reaction times, conversion of methyl chloride to hydrocarbons was achieved. Ethene (22.7%), propene (13.6%), and C4 compounds (5.8%) were the major higher hydrocarbons formed after 18 h on-stream (Figure 2). This is a significant breakthrough in methane activation especially in the direct conversion of methane to hydrocarbons using H-SAPO-34 as a catalyst at this relatively much lower temperature of 365 °C. To the best of our knowledge, this approach is found to be the most effective among all other methods reported so far on the transformation of methane to higher hydrocarbons over a solid catalyst. Zhang et al.[15] found that methyl chloride was converted to ethene (25%), propene (31%), and butenes (15%) at 450 °C over H-SAPO-34 using equimolar CH_3Cl/N_2 mixture. Svelle et al.[16] reported that approximately after 1 h on-stream at 350 °C with 1 bar of MeCl

Table 1. Chlorination over 7 g of H-SAPO-34 at 350 °C in the Presence of Moisture[a]

		product distribution (mol %)		
time (h)	conversion Cl_2 (mol %)	CH_3Cl	CH_2Cl_2	carbon balance (%)
0.5	87.3	100		100
1	88.9	100		99
2	91.7	100		97
18	83.0	60.3[b]	0.4	96
22	81.0	52.9[b]	0.3	96

[a] $CH_4/Cl_2/N_2/H_2O$ = 10:1:1.3:0.3. Total flow: 420 mL/h·g. [b] The rest is made of higher hydrocarbons; see Figure 2.

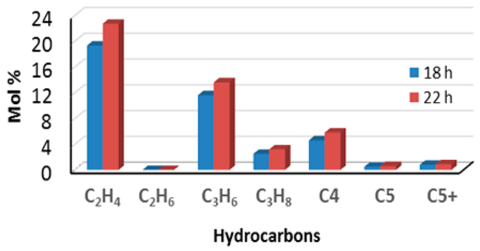


Figure 2. Hydrocarbon phase composition in the chlorination of methane over H-SAPO-34 at 350 °C after 18 and 22 h on-stream in the presence of moisture; 7 g of catalyst. $CH_4/Cl_2/N_2/H_2O$ = 10:1:1.3:0.3. Total flow: 420 mL/min.

and a flow rate of 10 mL/min a product distribution of ethene (20%), propene (38%), C4 (25%), and C5+ (7%). Herein, we report a direct protocol for the conversion of methane to higher hydrocarbons through the halide over a solid catalyst at a relatively low temperature of 365 °C.

The product distribution is sensitive to the reaction conditions. The presence of methyl chloride as the sole product during the first 2 h (Table 1) suggested an induction period for the production of higher hydrocarbons as observed by Svelle et al.[16] in the conversion of methyl halides to hydrocarbons. The GC of the product mixture also clearly shows the selective formation of methyl chloride. After 18 h on-stream, carbon deposits were visible on the catalyst as reported by several authors,[15,16] which explains the drop in the carbon balance.

The bromination of methane was carried out at 345 and 365 °C at different H-SAPO-34 loadings with a methane flow rate between 43 and 216 mL/g·h and methane to bromine molar ratio of 10.3:1. The conversion of bromine and the selectivity of the products were affected by both the catalyst loading and the temperature. Reaction with 3 g of catalyst at 365 °C for 3 h gave methyl bromide as the sole product as seen from ^{1}H and ^{13}C NMR of the product mixture (Figures 3 and 4). However, a blank reaction in the absence of the catalyst produced methyl bromide, methylene bromide, and bromoform, typical of a free radical process.[12,17] In the presence of the catalyst, the conversion of bromine increases with temperature, and at a given temperature, the conversion increases with an increase in the amount of catalyst. At 345 °C with 10 g of catalyst and a contact time of 83 s, the conversion of bromine was 38.6% with methyl bromide as the sole product (Scheme 3).

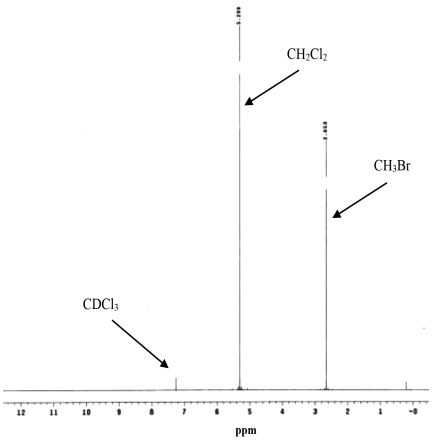


Figure 3. ^{1}H NMR of the product mixture in $CDCl_3$ (with CH_2Cl_2 as internal standard) after bromination of CH_4 over H-SAPO-34 at 144 mL/g·h, 365 °C, 3 h on-stream.

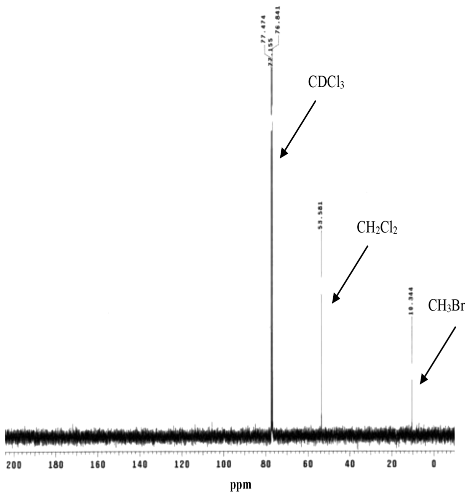
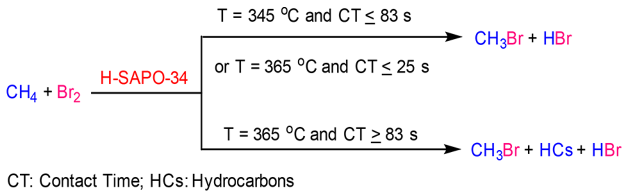


Figure 4. ^{13}C NMR of the product mixture in $CDCl_3$ (with CH_2Cl_2 as internal standard) after bromination of CH_4 over of H-SAPO-34 at 144 mL/g·h, 365 °C, 3 h on-stream.

Scheme 3. Methane Bromination over H-SAPO-34



At 365 °C, the conversion of bromine increased from 41.2% to 48.9% and 61.8% with a change in the amount of catalyst from 2 g of 1:1 catalyst−silica gel mixture to 3 g of catalyst and 10 g of catalyst, respectively. The selectivity remained 100% for both reactions using 1 g of catalyst (mixed with 1 g of silica, contact time 17 s) and 3 g of catalyst (contact time 25 s) (Scheme 3). As the amount of catalyst was increased to 10 g, a mixture of higher hydrocarbons was formed including liquid ones. As in the case of chlorination, methane could be directly converted to higher hydrocarbons at 365 °C via the in situ formed methyl bromide using bromine as an oxidant and H-SAPO-34 as a catalyst near atmospheric pressure. H-SAPO-34 contains bridging OH groups {SiO(H)Al} acting as Brønsted acid sites, which are responsible for the activity of the silicoaluminophosphates.[18,19] As suggested in the case of the electrophilic chlorination of methane with chlorine over aluminosilicate zeolites,[13] bromine is also activated on the Brønsted acid site in the pores of the zeolites to form the reactive electrophilic bromooxonium ion species through a transitional form in which the bromine atom would be covalently coordinated to the oxygen, making it capable of reacting with methane to yield methyl bromide.

The presence of Lewis acid sites in the SAPO cannot be excluded. These Lewis acid sites are extra-framework of aluminum or aluminum still partially bonded to the framework,[18−22] and under the reaction conditions they can readily be formed by the action of the hydrogen bromide produced during the reaction on the framework and nonframework aluminum.[15,16]

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IR studies of NH_3 adsorption on H-SAPO-34 revealed the presence of Brønsted and Lewis acid sites of similar strength.[20] These Lewis acid sites can also polarize the bromine molecules and induce electrophilic bromination as suggested by Olah et al.[4b] for the halogenation of methane over oxyhalides, supported Lewis superacid catalysts, and superacidic sulfated zirconia-based catalysts.[14] When the contact time was increased to 83 s (10 g of catalyst) at 365 °C, methyl bromide formed in the course of the reaction was partially transformed to higher hydrocarbons (Table 2, Figures 5 and 6, and Scheme 3).

Table 2. Bromination of Methane over H-SAPO-34[a]

			product distribution (mol %)			
catalyst wt (g)	T (°C)	conv. Br_2 (mol %)	CH_3Br	CH_2Br_2	$CHBr_3$	carbon balance (%)
10	345	38.6	100			100
0	365	57.8	81.0	12.6	6.4	99
1[b]	365	41.2	100			100
3	365	48.9	100			100
10	365	61.8	36.4[c]			98

[a] CH_4/Br_2 molar ratio 10.3:1. Methane flow rate 7.2 mL/min. Three h on-stream. [b] 1 g of H-SAPO-34 mixed with 1 g of silica gel. [c] The rest is made of higher hydrocarbons; see Figures 5 and 6.

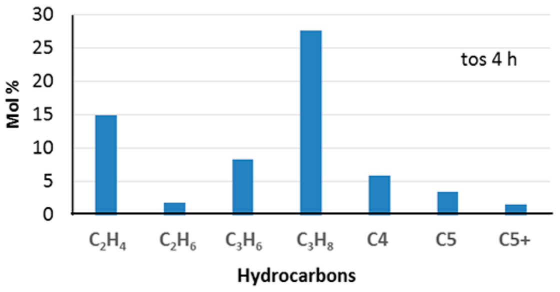


Figure 5. Hydrocarbon phase composition in the bromination of methane over H-SAPO-34 at 43.2 mL/g·h (10 g of H-SAPO-34), 365 °C, 4 h on-stream.

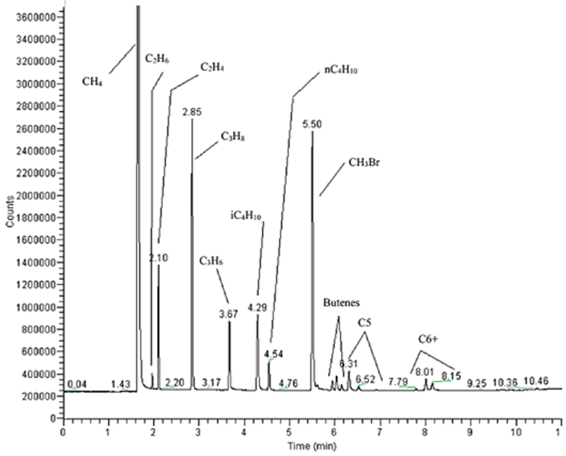


Figure 6. FID chromatogram of the bromination of CH_4 over of H-SAPO-34 at 43.2 mL/g·h (10 g of H-SAPO-34), 365 °C, 4 h on-stream.

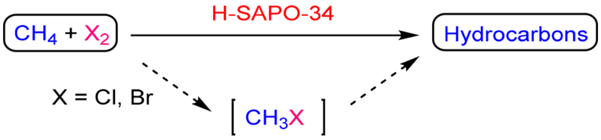
Linear alkanes (ethane, propane, n-butane), branched alkanes (2-methylbutane, 2,3-dimethylbutane, 3-methylpentane), and olefins (ethene, propene, 2-butene) were among the identified products. In this case, propane (27.6%), ethene (15.0%), and propene (8.3%) were the major products in contrast to the mixture of ethene and propene obtained when a mixture of methyl bromide and helium was passed over H-SAPO-34 at 0.1 bar.[15b] A hydrocarbon pool mechanism has been invoked to explain the formation of the products observed in the methanol or methyl halides to hydrocarbon reactions.[4a,15a,20,23−25] Wei et al.[15b] using FTIR found that the first step in the chloromethane conversion to hydrocarbons over H-SAPO-34 was the formation of surface methoxy groups from the dehalogenation of methyl chloride on the Brønsted acid site to give HCl and methyl species bonded to the oxygen. While the carbon balance was almost 100% at 345 and 365 °C for amounts of catalyst from 0 to 3 g, it fell to 98% for 10 g of catalyst and carbon deposits were visible on the catalyst after the reaction. Svelle et al.[16] found that the deactivation of the catalyst due to coke and polyaromatics depends on the reaction temperature in the conversion of methyl chloride and methyl bromide to hydrocarbons over H-SAPO-34. They observed a slow deactivation after exposure of the catalyst to the methyl halides at 350 °C, and methylbenzene isomers predominated inside the cavities of the catalyst with about 3% of coke deposits using 10% methyl bromide in helium after 0.5 h of reaction. At high temperature, the deactivation was severe and naphthalene derivatives were present in large amounts. Highly substituted benzene and cyclopentadiene derivatives were also found in the hydrocarbon mixture during the condensation of methyl bromide over $AlBr_3$ in a closed vessel.[8] In the latter case, propane was among the major products formed.

Under the reaction conditions studied, H-SAPO-34 with a catalyst loading of 3 g exhibited good stability with time. No carbon deposits were observed at 345 °C, though the catalyst turned slightly gray at 365 °C after 15 h on-stream. The increase of bromine conversion with temperature may be explained by a decrease in the activation energy and an increase in the formation of Lewis acid sites as already mentioned and/or coke formation, which induces a long contact time. It was shown in the case of MTO reaction over H-SAPO-34 that coke reduced the diffusivity of dimethyl ether and enhanced the formation of olefins.[25]

CONCLUSION

In conclusion, we have shown that at ambient pressure and moderate temperatures (345−365 °C) using chlorine or bromine as oxidant H-SAPO-34 is an effective and stable catalyst capable of converting methane to methyl halide or directly to higher hydrocarbons in one step (Scheme 4) simply by altering the reaction conditions. In previous cases, the conversion of methane to useful chemicals and fuels over solid catalysts proceeded at high temperatures or at least in two steps that require very different reaction conditions. When the activation of methane is achieved at high temperatures, the desired products, which are more reactive, undergo further

Scheme 4. One-Step Conversion of Methane to Hydrocarbons over H-SAPO-34



transformations to an undesired mixture of compounds. In this new protocol, the direct transformation to higher hydrocarbons is made possible through one-pot halogenation of methane to methyl halide and its oligomerization to hydrocarbons successively over H-SAPO-34 at the same temperature. Formation of methyl halide and hydrocarbons can be fine-tuned by changing the contact time. Short contact times favored the formation of the methyl halide, while long contact times allowed the in situ formation of hydrocarbons mainly in the C_2-C_6 range.

In the future, this approach would promote significant operational cost savings with further improvements in the conversion of methane to hydrocarbons in high yields with feasible low-cost reoxidation of the acid halide to halogen. Detailed studies are underway to explore more in depth the use of zeolites including metal-modified ones, particularly aluminosilicate phosphates for the direct conversion of methane to valuable chemicals via halogenation/oxidative condensation protocol.

EXPERIMENTAL SECTION

Materials. H-SAPO-34 (Al + P/Si = 5.57) was generously provided by UOP in the powder form. The preparation of the catalyst has been described earlier.[26] The chemical composition of catalyst was $(Si_{0.14}\,Al_{0.55}\,P_{0.30})\,O_2$ with 50% of the particles smaller than 1.2 μm. The acid density of 1.38 acid site per cage was determined by NH_3-TPD adsorption. The surface area (438 m^2/g) of the catalyst degassed at 673 K for 12 h was measured using NOVA 2200e Surface Area and Pore Size Analyzer; the pore diameter was 37.2 Å, and the pore volume was 0.20 cc/g.

Activation of Catalyst and Halogenation Procedure. Experiments were performed using a vertical 620 mm long 9 mm i.d. quartz tubular reactor. In a typical experiment, 3 g of catalyst was placed in the reactor between two quartz wool plugs. All parts were shielded from light. The catalyst was heated in air from room temperature to 500 °C at a rate of 3 °C/min and kept for 1 h at that temperature. Then the catalyst was cooled down to the reaction temperature under nitrogen flow. Methane flow, controlled by a calibrated mass flow controller (Aalborg), entrained bromine vapor from a bromine reservoir maintained at 2 °C to give a continuous supply of methane−bromine mixture in a ratio of 10.3:1. For bromination reactions, after 1 h on-stream, the products from the exit of the reactor were collected for 2 h in a solution of $CDCl_3$ kept at around −60 °C and analyzed by NMR (AS400 MHz Oxford) using dichloromethane as an internal reference. The connection from the exit of the reactor to the sample collector was heated at 150 °C to avoid condensation of the products. The flow out from the $CDCl_3$ trap was passed in a 5 M NaOH aqueous solution and measured using a flow meter. Samples were also taken at the entrance of the reactor and at the exit before and after the aqueous sodium hydroxide solution trap and analyzed off-line on two ThermoFiningan Trace GCs: one equipped with FID and TCD detectors using a 30 m Carboxen 1010 PLOT column from Supelco and the other with a FID detector using a 30 m GS-GASPRO column from Agilent. For chlorination reactions, N_2 was used as an internal reference and samples were only analyzed and quantified by GC. When moisture was added during chlorination, methane was passed into the water reservoir maintained at 22 °C before combining with chlorine. For catalyst loadings of 5 g and above, the maximum pressure observed in the system did not exceed 30 psi.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b10725.

Additional experimental details (PDF)

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Notes

The authors declare no competing financial interest.

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