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Simultaneous Conversion of Methane and Methanol into Gasoline over Bifunctional Ga-, Zn-, In-, and/or Mo-Modified ZSM-5 Zeolites**

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In response to increased energy demands, worldwide efforts have been made over the past 2–3 decades to develop alternative methods for the conversion of methane (a main constituent of natural gas, coal-bed gas, and biogas) into value-added products. These include ethylene (by oxidative coupling of methane),[1–3] syngas (by partial oxidation with or without simultaneous steam- and/or CO_2-mediated methane reformation),[4–8] and gasoline/liquid hydrocarbon fuels[9–14] that involve either oxidative[1–10] or nonoxidative[11–15] methane activation. As methane and carbon dioxide are key greenhouse gases responsible for global warming, the current industrial practice of emission and/or flaring of produced methane will be banned in the near future. The methane produced in remote places must therefore be converted into easily transportable energy sources like liquid hydrocarbon fuels at the sites of methane production. The most important approach for the transformation of methane into liquid hydrocarbons is the well-established and already commercially proven route:[16] methane→syngas→methanol→gasoline, based on the methanol-to-gasoline (MTG) process developed by Mobil.[16–18] In 1985, Mobil successfully operated a commercial plant in New Zealand for MTG conversions. However, its operation had to be discontinued as a result of unfavorable process economics.[18–20] The cost of the syngas production step (by steam reforming) is about twice the cost of the MTG production step.

The MTG process could become economically viable if it were possible to convert a significant portion of the methane into gasoline without the intermediate steps of conversion into syngas and methanol. Herein, we show that this very difficult goal can be met through the nonoxidative activation of methane and its simultaneous conversion with methanol into gasoline-range hydrocarbons over bifunctional Ga-, In-, Zn-, and/or Mo-modified ZSM-5 type zeolites that have both dehydrogenation and acid functions. We also show that the amount of methane converted can be equimolar to the amount of methanol converted in this novel process, depend-

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ing on the specific conditions. The conversion of methane to higher hydrocarbons was confirmed by using ^{13}C-labeled methanol and analysis of the reaction products by GC–MS. This work has the potential to revolutionize the methane-to-liquid hydrocarbons (MTL) conversion technology through the modified MTG process of Mobil.

The results in Figure 1, Figure 2, and Table 1 clearly indicate that methane is nonoxidatively activated and converted at low temperature ($<600\,^{\circ}C$) during methanol conversion over the bifunctional zeolite catalysts. However, methane is not activated/converted over H-ZSM-5; instead, it is produced in appreciable quantity (Figure 2). The simultaneous conversion of methane results in a significant change in the hydrocarbon product distribution relative to that of the conventional MTG process. Furthermore, the formation of individual $C_{\geq 2}$ hydrocarbons is increased markedly, as shown in Figure 1 and Table 1. The liquid hydrocarbons formed are mainly C_{7-12} aromatic compounds. The formation of benzene (the presence of which is undesirable because of its toxicity) was very small. In the absence of methane, an appreciable amount of methane is produced in the aromatization of methanol. Therefore, the presence of methane as a coreactant in our process is beneficial, as the aromatization of methanol results in no net formation of methane. It is of great practical interest that the amount of methane converted per mole of methanol in the feed could meet or exceed 1 mol, depending on the process temperature and methane/methanol ratio in the feed (Figure 2). The required methanol itself can be produced from methane through a well-established technology ($CH_4 \rightarrow$ syngas $\rightarrow$ methanol). Similarly, methane can also be activated and converted over bifunctional zeolite catalysts during the aromatization of other organic oxygenates, such as ethanol (which can be produced from renewable sources) and dimethyl ether (produced directly from syngas). Notably, Figure 1 illustrates that the hydrocarbon product distribution in the aromatization process presented herein is strongly influenced by the bifunctional zeolite, the oxygenate (methanol, ethanol, or dimethyl ether) used in the process, and the presence of methane in the feed. However, such strong influences are not observed in the aromatization of oxygenates over the monofunctional (acidic) zeolite (H-ZSM-5).

The H-GaAl-ZSM-5 (which is highly acidic and contains finely dispersed gallium oxide species) performs much better than the catalyst prepared through external impregnation of either the gallium, zinc, indium, or molybdenum oxide species on H-ZSM-5. However, the performance of the molybdenum, gallium, and indium oxide-impregnated H-ZSM-5 was

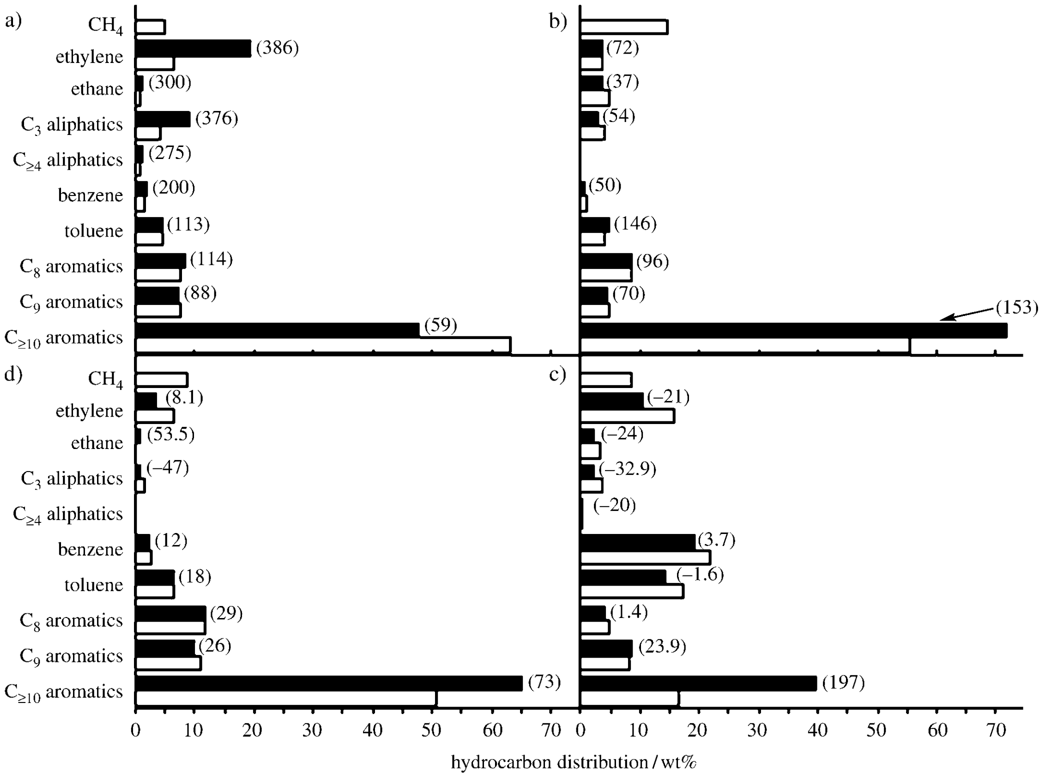


Figure 1. Distribution of hydrocarbons formed in the aromatization of a) methanol over H-GaAl-ZSM-5 at 550 °C, b) methanol over Mo-Zn/H-ZSM-5 at 500 °C, c) ethanol over H-GaAl-ZSM-5 at 625 °C, and d) dimethyl ether (DME) over H-GaAl-ZSM-5 at 550 °C in the presence (solid bars) and absence (open bars) of methane. $CH_4/(CH_3OH$ or DME$) = 15.0{:}1$, $CH_4/C_2H_5OH = 10{:}1$, $CH_4/N_2 = 8.5{:}1$, and gas hourly space velocity (GHSV), measured at 0 °C and 1 atm = 1050 $cm^3\,g^{-1}\,h^{-1}$. Values in round brackets correspond to the percentage increase in the formation of a particular hydrocarbon as a result of the presence of methane. The conversion of methanol, ethanol, or DME was 100%. In the presence of oxygenate, the amount of methane converted was 0.96 and 1.19 mol/mol CH_3OH for H-GaAl-ZSM-5 and Mo-Zn/H-ZSM-5, respectively, and 0.8 and 0.94 mol/mol CH_3CH_2OH and DME, respectively. In continuous operation for 7 h, both catalysts showed no significant change in catalytic activity for methane conversion.

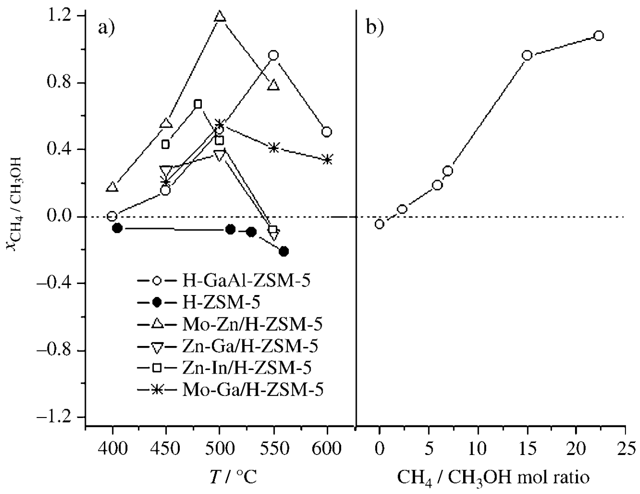


Figure 2. a) Moles of methane converted per mole of methanol (X_{CH_4/CH_3OH}) in the simultaneous aromatization of methane and methanol over H-GaAl-ZSM-5 and H-ZSM-5 ($CH_4/CH_3OH = 15:1$, $CH_4/N_2 = 8.5:1$, GHSV = 1050 $cm^3 g^{-1} h^{-1}$); Mo-Zn/H-ZSM-5 ($CH_4/CH_3OH = 14.1:1$, $CH_4/N_2 = 8.5:1$, GHSV = 1050 $cm^3 g^{-1} h^{-1}$); Zn-In/H-ZSM-5 ($CH_4/CH_3OH = 12.72$, $CH_4/N_2 = 8.5:1$, GHSV = 1200 $cm^3 g^{-1} h^{-1}$); Mo-Ga/H-ZSM-5 ($CH_4/CH_3OH = 13.75:1$, $CH_4/N_2 = 7.3:1$, GHSV = 1200 $cm^3 g^{-1} h^{-1}$); and Zn-Ga/H-ZSM-5 ($CH_4/CH_3OH = 5.9:1$, $CH_4/N_2 = 7.2:1$, GHSV = 1200 $cm^3 g^{-1} h^{-1}$). b) Effect of the ratio of CH_4/CH_3OH in the feed on moles of methane converted per mole of methanol in the simultaneous aromatization of methane and methanol over H-GaAl-ZSM-5 at 550 °C ($CH_4/N_2 = 8.5:1$, GHSV = 1050 $cm^3 g^{-1} h^{-1}$). Methanol conversion in all cases was 100 %.

Table 1: Influence of methane on the process formation of C_{2-12} hydrocarbons with H-GaAl-ZSM-5 and Mo-Zn/H-ZSM-5 zeolite catalysts.

	Reaction conditions		X_{CH_4/CH_3OH}[a]	Δ (C_2–C_{12} hydrocarbons) [%][b]
T [°C]	CH_4/CH_3OH [mol ratio]	GHSV [$cm^3 g^{-1} h^{-1}$]		
		catalyst: H-GaAl-ZSM-5		
500	15.0:1	1050	0.52	49
550	15.0:1	1050	0.96	108
550	7.0:1	1050	0.27	31.8
550	15.0:1	2100	0.79	83
		catalyst: Mo-Zn/H-ZSM-5		
450	14.1:1	1050	0.55	53
500	14.1:1	1050	1.19	126
550	14.1:1	1050	0.78	77
500	7.1:1	1050	0.29	30
500	14.1:1	2100	0.55	47

[a] Moles methane converted per mole methanol. [b] Increase due to the presence of methane.

improved appreciably after the addition of zinc oxide to the catalyst. The catalytically active Mo-containing species may be Mo_2C and/or MoO_xC_y.[21]

Low-temperature (≤ 600 °C) conversion of methane to aromatic hydrocarbons is not thermodynamically feasible, as $\Delta G > 33.4\ kJ\,mol^{-1}_{carbon}$. However, if this conversion is carried out in the presence of methanol over the bifunctional zeolite catalysts, which have strong protic acid and dehydrogenation sites, it becomes thermodynamically favorable as a result of the simultaneous conversion of methane and methanol. (For example, $\Delta G = -8.8$, -15.5, and $-22.2\ kJ\,mol^{-1}$ at 400, 500, and 600 °C, respectively, for one mole of methane converted per mole of methanol.)

In the absence of methanol and/or the absence of bifunctional sites on the zeolite catalyst, there was no conversion of methane. The negative values observed for the ratio of (methane converted)/(methanol converted) with the H-ZSM-5 zeolite (Figure 2 a) and in the absence of methane (Figure 2 b) indicates the net formation of methane to a significant extent. An temperature optimum is observed for obtaining the highest ratio of (methane converted)/(methanol converted), which depends on the bifunctional zeolite used (Figure 2 a). This can be explained by the expected competition between the formation of methane from methanol by cracking reactions (which have a higher rate at higher temperature) and the activation/conversion of methane, which has a lower rate at lower temperature. The ratio of (methane converted)/(methanol converted) is, however, increased markedly with an increase in the methane/methanol ratio in the feed (Figure 2 b).

The activation and conversion of methane in the process was confirmed by using ^{13}C-labeled methanol and analysis of the aromatic hydrocarbons formed by GC–MS. The MS data of toluene and xylene produced in the presence and absence of methane in the feed are compared in Figure 3. The mass spectra clearly reveal the formation of unlabeled toluene (formed from methane alone) and partially labeled aromatic compounds (formed from both methane and methanol) in the aromatization of $^{13}CH_3OH$ over the H-GaAl-ZSM-5 and Zn-In/H-ZSM-5 catalysts in the presence of methane. Methane appears to act as an alkylating agent in the formation of methylbenzenes and methylnaphthalenes. Indeed, upon passing a mixture of methane and benzene ($CH_4/C_6H_6 = 12.5:1$) over the H-GaAl-ZSM-5 zeolite at 550 °C, the alkylation of benzene was observed in the formation of toluene and xylenes in significant quantity (with 1.0 % conversion of benzene).

We propose the following mechanism for the activation and conversion of methane during the aromatization of methanol over the bifunctional zeolite catalysts Z, which have strong Brønsted acid sites and nonframework gallium, zinc, and/or indium oxide species, with or without Mo_2C or MoO_xC_y species as dehydrogenation sites in the zeolite channels.

Methanol aromatization [Eq. (1)]:

$$\begin{aligned} &Z^-H^+ + CH_3OH \rightleftharpoons Z^-[CH_3OH_2]^+\ \mathbf{I} \rightarrow \\ &Z^-H^+ + H_2O + C_{1-12}\ \text{hydrocarbons} \end{aligned} \qquad (1)$$

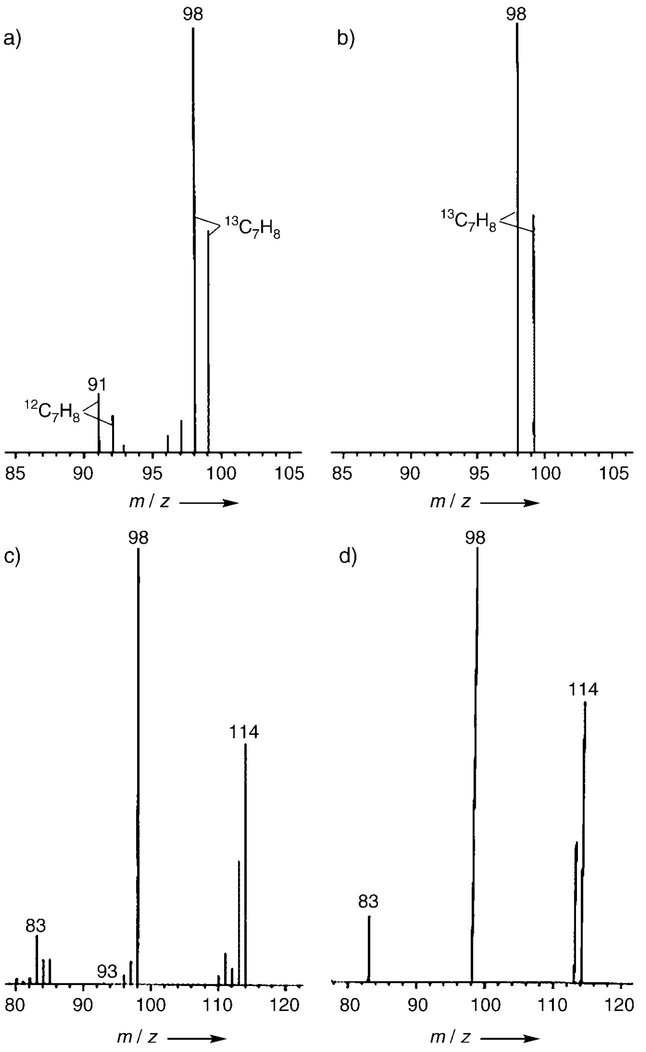
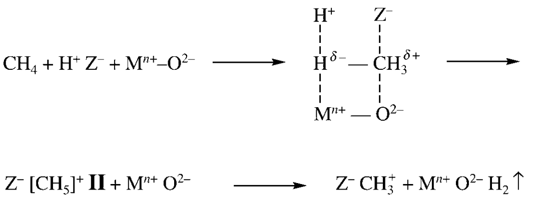


Figure 3. GC–MS spectra of toluene and xylene formed in the aromatization of ^{13}C-labeled methanol ($^{13}CH_3OH$) over the H-GaAl-ZSM-5 zeolite in the presence and absence of methane under identical conditions (at 550 °C and GHSV = 1050 $cm^3 g^{-1} h^{-1}$). Reaction conditions:
a) $CH_4/^{13}CH_3OH = 14.7{:}1$, $CH_4/N_2 = 7.3{:}1$, toluene, $t_{ret} = 4.56$ min;
b) $CH_4/^{13}CH_3OH = 0{:}1$, $N_2/^{13}CH_3OH = 16.7{:}1$ toluene, $t_{ret} = 4.56$ min;
c) $CH_4/^{13}CH_3OH = 14.7{:}1$, $CH_4/N_2 = 7.3{:}1$, xylene, $t_{ret} = 7.68$ min;
d) $CH_4/^{13}CH_3OH = 0{:}1$, $N_2/^{13}CH_3OH = 16.7{:}1$ xylene, $t_{ret} = 7.68$ min.
t_{ret} = retention time.

Methane activation and conversion (M = Ga, Zn, or In; X = Mo_2C or MoO_xC_y species) [Eq. (2)–(7)]:

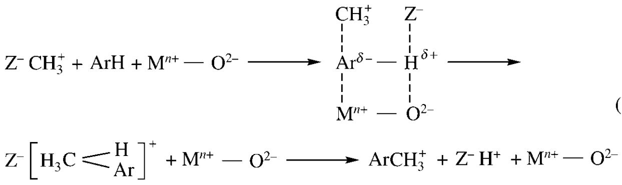


$$CH_4 + H^+Z^- + M^{n+}\text{–}O^{2-} \longrightarrow \begin{array}{ccc} H^+ & & Z^- \\ \vdots & & \vdots \\ H^{\delta-} & — & CH_3^{\delta+} \\ \vdots & & \vdots \\ M^{n+} & — & O^{2-} \end{array} \longrightarrow$$

$$Z^-[CH_5]^+\,\mathbf{II} + M^{n+}O^{2-} \longrightarrow Z^-CH_3^+ + M^{n+}O^{2-}\,H_2\uparrow \qquad (2)$$

$$Z^-CH_3^+ \rightarrow Z^-H^+ + CH_2 \qquad (3)$$

$$2\,CH_2 \rightarrow C_2H_4 \xrightarrow[\text{oligomerization aromatization}]{Z^-H^+ + Mn\text{–}O_2^-} \begin{array}{l}\text{aliphatics}\\ \text{aromatics and } H_2\end{array} \qquad (4)$$



$$Z^-CH_3^+ + ArH + M^{n+}—O^{2-} \longrightarrow \begin{array}{ccc} CH_3^+ & & Z^- \\ \vdots & & \vdots \\ Ar^{\delta-} & — & H^{\delta+} \\ \vdots & & \vdots \\ M^{n+} & — & O^{2-} \end{array} \longrightarrow$$

$$Z^-\left[H_3C{<}\begin{array}{l}H\\Ar\end{array}\right]^+ + M^{n+}—O^{2-} \longrightarrow ArCH_3^+ + Z^-H^+ + M^{n+}—O^{2-} \qquad (5)$$

$$X + Z^-CH_3^+ \rightarrow XCH_2 + Z^-H^+ \qquad (6)$$

$$2\,XCH_2 \rightarrow 2\,X + C_2H_4 \qquad (7)$$

Methane is activated mostly as a result of the combined action of the metal oxide species and zeolitic protons, both present at the channel intersections in close proximity to each other. Our earlier studies on the alkane and alkene aromatization over Ga-modified ZSM-5 zeolites also revealed that the zeolitic protons and nonframework gallium oxide species work in cooperation with each other.[22] Methyl cations are likely to be produced through the formation of pentacoordinated carbocations **II**, similar to that proposed earlier by Olah.[23] As no methane conversion is observed in the absence of methanol and/or the bifunctional sites, activation of the H–CH_3 bond and formation of the pentacoordinated carbocations **II** are expected to be facilitated by the nonframework metal oxide species in the presence of oxonium cations **I** and/or carbenium ions formed from the olefins produced from methanol.

The highly unstable methyl cations are expected to be stabilized by the zeolitic framework negative charge (Z^-) as $Z^-CH_3^+$. The role of the metal oxide/carbide species (gallium, indium, and zinc oxides, MoC_2 or MoO_xC_y species) present at the zeolite channel intersections in close proximity to the zeolite protons is not only to facilitate the methane activation but also to facilitate recombination of hydrogen adatoms[24] formed during the C–H bond activation [Eq. (2)]. One mole of H_2 (which appears in the products) is produced per mole of methane activated. The mechanism explains the observed direct conversion of methane into toluene and incorporation of ^{12}C from methane into the aromatics produced from $^{13}CH_3OH$. A very high concentration of methane relative to that of higher hydrocarbons (and consequently relative to methanol) is essential for the formation of a significant amount of methyl cations [by Eq. (2)] and/or pentacoordinated carbocations **II**. This is consistent with the observations; the methane converted per mole of methanol converted is increased markedly with an increase in the methane/methanol ratio in the feed (Table 1, Figure 2b).

Methanol aromatization is highly exothermic ($\Delta H_r \approx -264\,kJ\,mol^{-1}$ (*m*-xylene)), and this is one of the major concerns about the MTG process of Mobil. However, in our process, the simultaneous endothermic conversion of methane and exothermic aromatization of methanol over the same catalyst are coupled, which renders the process highly energy efficient. It also eliminates the possibility of process runaway. The other important advantages of this process are: 1) the oxygenate additive (methanol or dimethyl ether) in the methane feed can be produced from methane itself through a well-established technology (methane→syngas→methanol or dimethyl ether); 2) the conversion of the additive is complete (100 %); 3) methane converted per mole of additive can be close to 1.0, hence the requirement of the additive is much smaller than that of the previous process involving higher hydrocarbons as the additive.[11–14] The process of high-temperature (> 700 °C) methane aromatization over Mo/H-ZSM-5 catalysts[21] is not technically feasible, as the catalyst is deactivated very rapidly. Because of the above highly attractive features, the process presented herein is expected to be much more feasible commercially. Further development of the bifunctional zeolite catalysts and optimization of the process conditions should lead to an economically feasible MTL technology which would not only eliminate the flaring of methane and associated natural gases but which would also satisfy increasing energy demands.

Experimental Section

A mixture of methanol (or ^{13}C-labeled methanol) vapors and premixed methane–N_2 (molar ratio $CH_4/N_2 = 8.5$) gas from a cylinder was passed over bifunctional Ga-, In-, Zn- and/or Mo-modified ZSM-5 (H-GaAl-ZSM-5 (Si/Al = 49.6, Si/Ga = 15.3, nonframework Ga = 0.65 mmol g^{-1}), Mo (2 %)–Zn (2 %)/H-ZSM-5, Zn (2 %)–In (2 %)/H-ZSM-5, Mo (2 %)–Ga (2 %)/H-ZSM-5, and Zn (2.3 %)–Ga (2.4 %)/H-ZSM-5) zeolite catalysts[25,26] in a tubular quartz reactor[11,26] at different reaction conditions. Before reaction, the Mo-containing catalyst was pretreated by passing a mixture of CH_4–H_2 (6 % H_2) over it at 550 °C for 4 h, whereas the other catalysts were pretreated in the presence of N_2 under similar conditions. The reaction products were analyzed by GC with thermal conductivity and flame ionization detectors connected in series, or by GC–MS. Methane conversion was determined by using nitrogen as an internal standard: (% CH_4 converted) = $\{[(CH_4/N_2)_{feed} - (CH_4/N_2)_{products}]/(CH_4/N_2)_{feed}\} \times 100$. In all runs, 100 % conversion of methanol to hydrocarbons and water was observed. The formation of carbon monoxide in the methanol conversion in the presence or absence of methane was negligible. Furthermore, no formation of carbon monoxide was detected upon passing a mixture of methane and steam over the bifunctional zeolite catalyst at 550 °C.

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