

# Evolution of C–C Bond Formation in the Methanol-to-Olefins Process: From Direct Coupling to Autocatalysis

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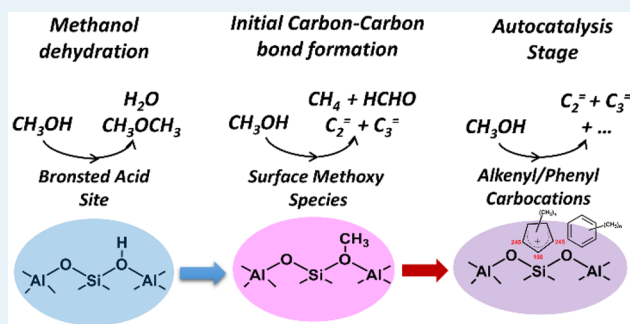
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## S Supporting Information

**ABSTRACT:** Methanol conversion during the induction period of methanol-to-olefin (MTO) process has been investigated by solid-state nuclear magnetic resonance (ssNMR), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), gas chromatography–mass spectroscopy (GC-MS), and time-of-flight mass spectroscopy (TOF-MS), over HSAPO-34 molecular sieve. The two-dimensional (2D) <sup>13</sup>C–<sup>13</sup>C MAS NMR spectra revealed the correlation of surface methoxy species (SMS) and dimethyl ether (DME)/methanol was enhanced with the temperature increase, supporting that the carbon–carbon (C–C) bond can be possibly formed through the direct coupling of SMS and the surface-adsorbed C1 reactant. The evolution of surface species was monitored continuously by the aid of in situ ssNMR and in situ DRIFTS. With the consumption of SMS, alkenyl or/and phenyl carbocations were formed and accumulated as the successive intermediates for methanol conversion. Based on these direct observations, we propose that the first C–C bond is derived from SMS-mediated DME/methanol activation while alkenyl/phenyl carbocations can take over SMS and convert methanol efficiently in the autocatalysis stage of the MTO process.

**KEYWORDS:** methanol to olefins, induction period, carbon–carbon bond, direct mechanism, autocatalysis



Since the reaction of methanol-to-hydrocarbon over zeolite was discovered by Mobil in 1977,<sup>1</sup> in the past four decades, the well-known methanol-to-olefins (MTO) process over SAPO-34 or ZSM-5 has obtained great success in industrialization, but some critical issues about the reaction mechanism are still under discussion. Chemical research of the MTO reaction mechanism was mostly focused on two aspects: (1) the formation of the first C–C bond and (2) the reaction pathway by which MTO proceeds in the efficient reaction stage. For the latter, some well-known indirect mechanisms have been proposed and widely acknowledged.<sup>2–5</sup> The general agreement have achieved that the efficient methanol reaction over zeolite or zeotype catalysts goes through the indirect pathways with cyclic organics or alkene intermediates as the co-catalyst. The detailed reaction route, the proceeding of alkenyl-based cycle or the phenyl-based cycle, is mainly determined by the acidity and topology of the catalysts used and varied with the operating conditions.<sup>6–9</sup> As for the former, the first C–C bond formation, although many direct mechanisms have been proposed, is still very controversial,

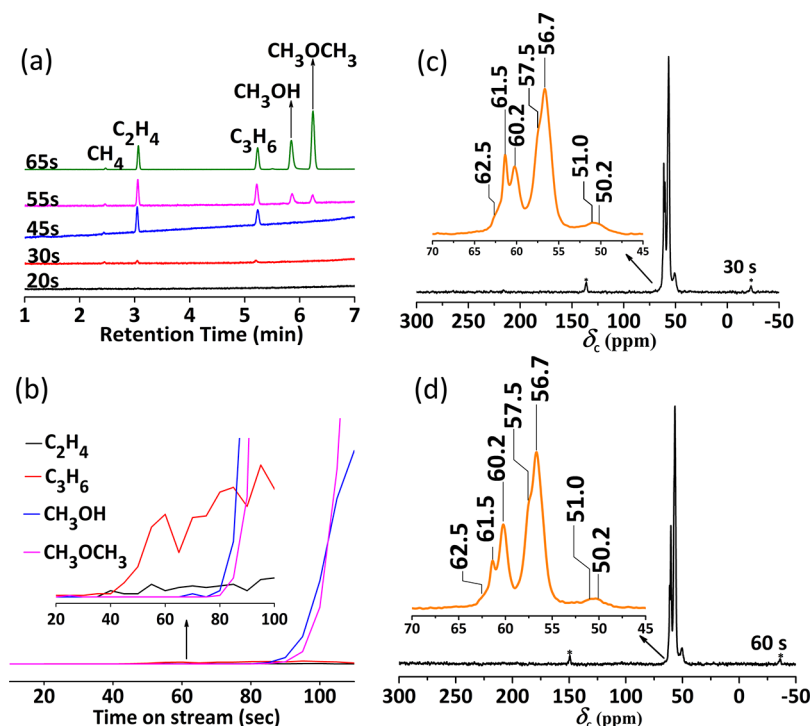
because of either the lack of experimental evidence or the ultrahigh theoretically calculated energy barrier.<sup>10–15</sup> At one time, impurities from the feedstocks and carrier gas, or the catalyst contaminations were once thought to be the source of the first C–C bond,<sup>16</sup> but the study of Hunger and co-workers indicated that trace amounts of organic impurities have hardly any influence on the formation of hydrocarbon pool (HCP) species.<sup>17</sup> They suggested the surface methoxy species (SMS) as an essential intermediate for the first C–C bond formation.<sup>18,19</sup> In very recent studies, some research groups have provided experimental or/and theoretical evidence for the feasibility of direct mechanisms.<sup>20–25</sup> Because of the lack of authentic experimental evidence and the complexity of the induction period reaction, an ongoing debate about the C–C bond formation remains, even to this day. The further conversion of the initial C–C bond to more-efficient

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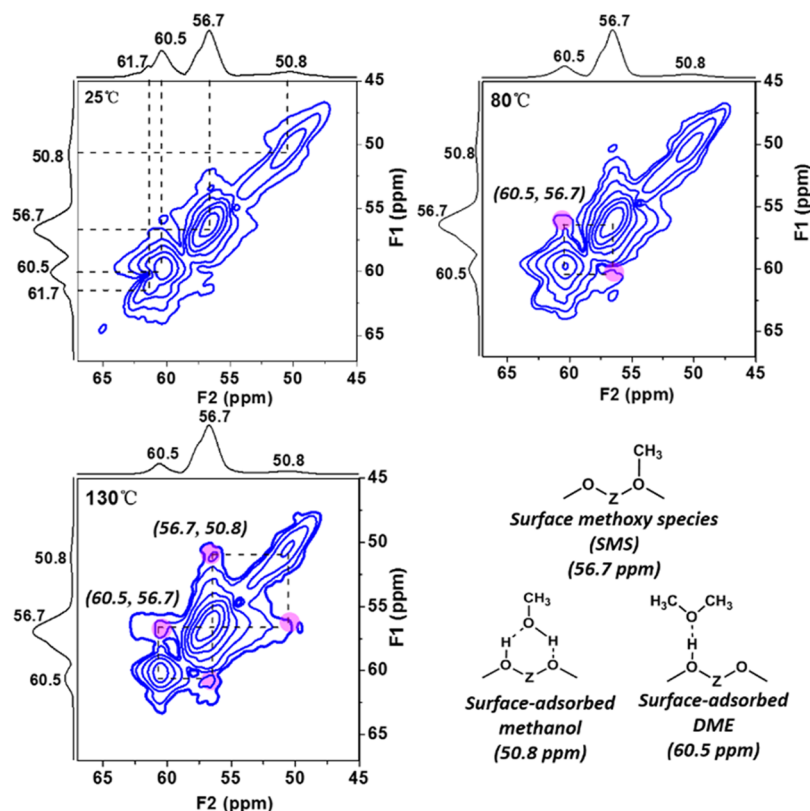
**Figure 1.** Initial effluent and catalyst surface species during methanol conversion over HSAPO-34 at 300 °C with a methanol weight hourly space velocity (WHSV) of 2.0 h<sup>-1</sup>: (a) GC-MS chromatograms of effluent products from 20 to 65 s; (b) real-time signals of methanol, DME, ethene, and propene monitored by TOF-MS; (c) <sup>13</sup>C CP/MAS NMR spectra of the HSAPO-34 catalyst recorded at room temperature after <sup>13</sup>C-methanol conversion at 300 °C for 30 s; and (d) <sup>13</sup>C CP/MAS NMR spectra of the HSAPO-34 catalyst recorded at room temperature after <sup>13</sup>C-methanol conversion at 300 °C for 60 s. Asterisk symbol (\*) indicates the spinning sideband.

intermediates has also not been clarified during the induction period of the MTO process.

In this work, through the aid of gas chromatography–mass spectrometry (GC-MS) and time-of-flight mass spectrometry (TOF-MS), solid-state nuclear magnetic resonance (ssNMR) spectroscopy, and diffusion reflectance infrared Fourier transformation spectroscopy (DRIFTS), methanol conversion has been thoroughly studied over HSAPO-34, the most important industrial catalyst of MTO process. Accompanied with the detection of the initial hydrocarbons, SMS was the only newly formed organic species on the catalyst surface, implying its very possible involvement in the formation of initial hydrocarbons. More importantly, the two-dimensional (2D) <sup>13</sup>C–<sup>13</sup>C PDS (proton-driven spin-diffusion) ssNMR spectra presented the pronounced correlation of SMS and the surface-adsorbed C1 reactants (DME/methanol) at enhanced operating temperature, suggesting that SMS-mediated C1 reactant conversion is a definite pathway for the initial C–C bond formation. Moreover, the evolution of surface organic species was continuously monitored by both in situ ssNMR and in situ DRIFTS. It was found that SMS was mainly formed and functioned during the initial reaction period. Once initial olefins were generated, alkenyl or aromatic species would be formed on the catalyst and take over SMS for DME/methanol conversion, according to the well-established indirect mechanisms.

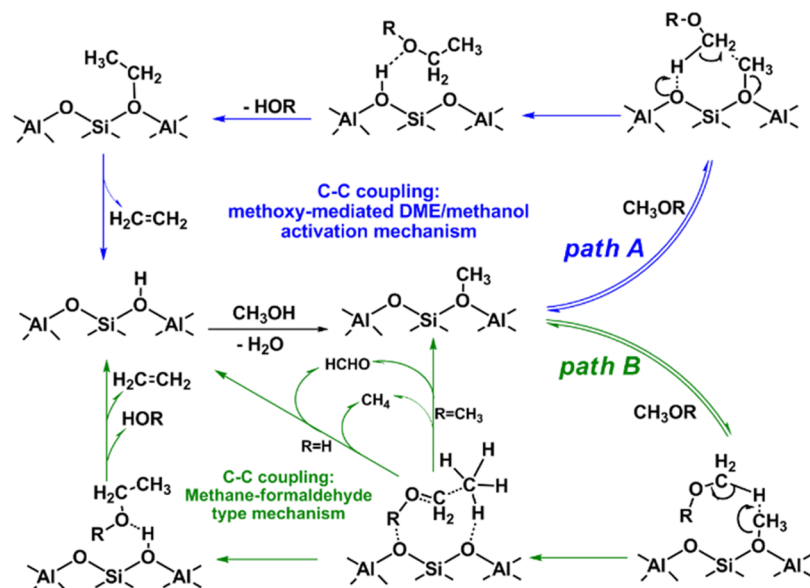
A methanol reaction performed over HSAPO-34 (catalyst characterization results are presented in Figures S1–S5 in the Supporting Information) at 300 °C was tracked with online GC-MS to detect the effluent compounds in the very initial reaction stage. As shown in Figure 1 a, no signal was presented on the gas chromatogram with methanol feeding for 20 s. After

30 s, trace amounts of methane, ethene, and propene were detected as the initial products and the peaks of ethene and propene were intensified at 45 s, while methanol and DME were still absent in the effluent during this period. Through the continued feeding of methanol until 55 s, methanol and DME could be detected among the effluent. The absence of methanol and DME in the effluent during the initial 45 s implied that the initially fed methanol and its dehydrated product DME remained on the surface of HSAPO-34 as strongly adsorbed species until methanol was in excess for the catalyst bed. A time-resolved TOF-MS was also used for the real-time monitoring of the effluent compounds (see Figure 1 b). Ethene and propene were almost simultaneously captured within ~35 s, while the appearance of DME/methanol was delayed, which was in agreement with the result from GC-MS. In such a short reaction time, methanol feeding gave rise to the initial formation of olefin products. The interaction of adsorbed reactant or the intermediate would be critical for revealing the initial C–C bond formation, so the reaction was stopped at 30 and 60 s and the methanol-reacted catalyst was quenched by liquid nitrogen and transferred as quickly as possible into the NMR rotor for <sup>13</sup>C CP/MAS NMR measurement. During the first 1 min (see Figures 1c and 1d), the signals at 62.5, 61.5, and 60.2 ppm are attributed to adsorbed DME on different Brønsted acid sites or in different configurations. Similarly, methanol adsorption also gives rise to the signals observed at 50.2 and 51.0 ppm. Despite the peak overlap, the signals at 56.7 and 57.5 ppm can still be recognized and assigned to SMS. SMS was the only newly formed surface species detected at the very beginning of the reaction, so the first C–C bond generation was supposed to be



**Figure 2.** ssNMR correlations of SMS, DME, and methanol on HSAPO-34. 2D  $^{13}\text{C}$ – $^{13}\text{C}$  MAS NMR spectra with a mixing time of 150 ms are recorded at 25, 80, and 130 °C after the MTO reaction for 60 s at 300 °C.

**Scheme 1. Plausible Reaction Pathways for the Formation of the Earliest-Detected Hydrocarbons during the Initial Stage of the MTO Reaction<sup>a</sup>**



<sup>a</sup>Path A is SMS-mediated DME/methanol activation and reaction for the formation of the initial ethene in MTO process; path B gives a feasible explanation for the formation of methane and formaldehyde and their further reaction as an alternative way of the initial generation of ethene.

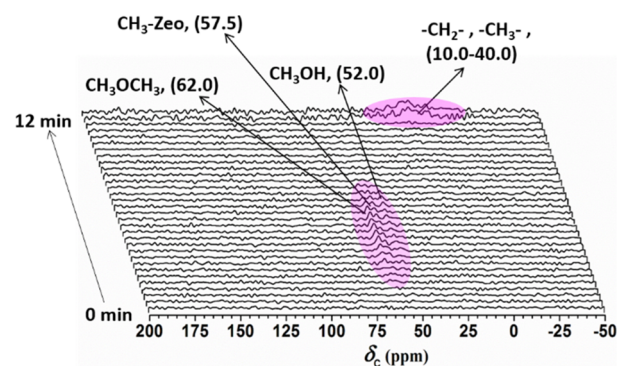
closely related to SMS as the critical intermediate for methanol/DME conversion to initial hydrocarbon products.

The 2D  $^{13}\text{C}$ – $^{13}\text{C}$  MAS NMR spectroscopy of the initial methanol reaction over HSAPO-34 (after feeding methanol for 60 s at 300 °C) was employed to study the feasibility of this chemical assumption. The spectra were recorded at 25, 80, and

130 °C with a mixing time at 150 ms to measure the possible interaction of the surface adsorbed C1 species. When it was measured at 25 °C, there is no cross-peak from the  $^{13}\text{C}$ – $^{13}\text{C}$  correlation (see Figure 2). Two cross-peaks between SMS at 56.7 ppm and DME at 60.5 ppm could be captured when the operation temperature was increased to 80 °C. By further

increasing the temperature to 130 °C, the correlation of SMS and methanol could be also captured and the correlation of SMS and DME was intensified. The intensification of the  $^{13}\text{C}$ – $^{13}\text{C}$  correlation between SMS and surface-adsorbed C1 reactant indicated the close spatial proximity and the stronger interaction at increased temperature. In this trend, once the temperature increased to a higher value, more closer spatial proximity may give rise to even stronger interaction between SMS and the adjacent DME/methanol. Weckhuysen and co-workers observed the correlation of the SMS and surface-adsorbed methanol, and suggested that chemical reactions have a tendency to occur and the C–C bond might be constructed between the correlated carbon atoms.<sup>21,25</sup> In this contribution, the correlation between SMS and DME could be established at relatively low temperature, implying a strong interaction, which held great potential for their further activation and reaction. In our recent work, the activated DME species has been successfully captured on HZSM-5 with in situ ssNMR spectroscopy.<sup>20</sup> SMS and the adjacent framework oxygen was proposed to work in an associative manner for the C1 reactant activation. In the present study, the observation of the correlation of C1 species on HSAPO-34 consolidates the strong interaction of SMS and C1 reactant and verifies the significance of SMS-mediated DME/methanol conversion for the initial generation of olefins. Plausible reaction pathways are suggested to elaborate the possible interaction and reaction of SMS and surface-adsorbed methanol and DME in spatial affinity (see Scheme 1). As shown in path A in Scheme 1, when SMS and the adjacent framework oxygen work together in an associative manner, the H atom of the DME/methanol would be donated to the negatively charged framework oxygen and a simultaneous methylation gives rise to a surface-adsorbed ethanol or methyl ethyl ether containing the first C–C bond. And then, ethene would be generated by the dehydration of the adsorbed ethanol or the decomposition of the methyl ethyl ether. In path B in Scheme 1, the electrophilic attack from SMS leads to another option, in which the adjacent DME/methanol could donate its H atom to SMS, and in this way, the adduct of methane and adsorbed formaldehyde would be generated. On one hand, methane and formaldehyde could be released into the gas phase as stable products, which is confirmed by the detection of GC-MS; on the other hand, the further transformation of methane and formaldehyde has been theoretically predicted to be energetically favorable to form a surface-adsorbed ethanol, according to the earlier proposed methane–formaldehyde mechanism.<sup>10,11</sup> All of these suggestions are based on the detection of the correlation of SMS and the adsorbed C1 reactant. The SMS-mediated methanol/DME conversion for C–C bond formation is the most crucial reaction for initial generation of olefins from methanol conversion on HSAPO-34.

To reveal the real-time evolution of the reaction mode of MTO over HSAPO-34 under real working conditions, the in situ ssNMR measurement of the continuous-flow  $^{13}\text{C}$ –methanol conversion was conducted in a rotor reactor at 300 °C. As shown in Figure 3, three signals appeared in the first few minutes. The peaks at 62.0 and 52.0 ppm were attributed to surface-adsorbed DME and methanol, respectively, while SMS gave rise to the signal at 57.5 ppm. The occupation of the catalyst surface by the three C1 species at the beginning of the reaction signified that the interaction of SMS and C1 reactants is responsible for the C–C bond formation during the very initial reaction stages. The reinforced correlation between SMS

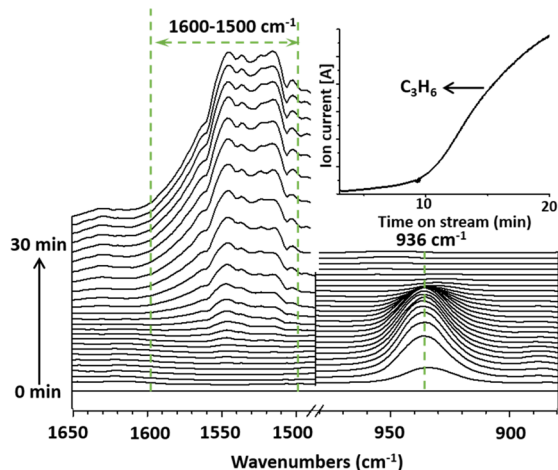


**Figure 3.** In situ  $^{13}\text{C}$  MAS NMR spectra recorded during  $^{13}\text{C}$ -methanol conversion over HSAPO-34 at 300 °C under flow conditions. The spectra were recorded every 20 s from 0 to 10 min and then every 60 s from 10 min to 12 min.

and DME/methanol with temperature increase has been confirmed by 2D  $^{13}\text{C}$ – $^{13}\text{C}$  MAS NMR studies of the surface C1 species at varied temperature. The proceeding of direct C–C bond coupling reaction was based on the strong interaction between the C1 species under the real reaction conditions. After feeding methanol for  $\sim 7$  min, these signals from C1 species started to decline and lost their intensity in the following reaction time. From 10 min, the signals from methyl or methylene carbon of higher hydrocarbons appeared at 10–40 ppm. Because of the limited recording time of each spectrum recorded in situ for a time-resolved monitoring, the NMR signals were not well-accumulated in situ between 7 min and 10 min. Actually, a detailed study with prolonged recording time indicated that, at a reaction time of  $\sim 6$  min, both aromatics (130.0–135.0 ppm) and polymethylcyclopentenyl carbocations (153.0, 245.0 ppm) already formed on the catalyst and could be detected by  $^{13}\text{C}$  CP/MAS NMR (see Figure S6 in the Supporting Information). The signals of aromatics and polymethylcyclopentenyl carbocations were intensified at a reaction time of 10 min (see Figure S7 in the Supporting Information), and, at this moment, polymethylbenzene carbocations were also generated with the appearance of the signals at 141.0, 189.0, and 198.0 ppm. These cyclic organics behave as important intermediates for methanol conversion in a more efficient pathway.<sup>6,7,26,27</sup> At the same time, SMS gradually quit the catalyst surface with its signal intensity decrease from 6 min to 10 min. Once the initial olefins are formed, the autocatalysis of MTO reaction will be rapidly triggered.<sup>13,28</sup> The initial olefins and the secondary products, alkenyl or phenyl species, which can be generated from the reactions of olefins conducted on Brønsted acid sites, such as oligomerization, cyclization, hydrogen transfer, and aromatization, will take over SMS as the successive intermediates for MTO reaction on the HSAPO-34 surface. With the formation and accumulation of these more reactive intermediates, methanol will be efficiently transformed via the indirect route and present an exponential growth in conversion rate, which is characteristic of the autocatalysis reaction (see Figure 1 b).

The in situ DRIFT experiment of methanol conversion over HSAPO-34 was conducted in a cell reactor. The characteristic IR absorbance peak of SMS over HSAPO-34 was confirmed by the experiment with a temperature-programmed increase in advance (see Figure S8 in the Supporting Information). With the increase in temperature, the changes in the intensity of the

bands at 2977 and 2866  $\text{cm}^{-1}$  from the stretching vibration absorbance of C–H bond in SMS were consistent with that of the band at 940  $\text{cm}^{-1}$  from stretching vibration absorbance of C–O bond in framework-bound SMS. The spectra recorded during continuous methanol conversion over HSAPO-34 at 300  $^{\circ}\text{C}$  is shown in Figure 4. Upon feeding methanol onto the



**Figure 4.** In situ DRIFT spectra recorded during methanol conversion over HSAPO-34 at 300  $^{\circ}\text{C}$ . The spectra were recorded from 0 to 30 min.

catalyst, the signal of SMS appeared at the beginning and its intensity increased from 0 to 7 min, then declined, and finally lost its intensity after  $\sim 15$  min. With the intensity decline and disappearance of SMS signal, the absorbance bands between 1600  $\text{cm}^{-1}$  and 1500  $\text{cm}^{-1}$ , which are generally attributed to aromatic and allylic cationic species<sup>29–31</sup> sharply increased in intensity with prolonging the reaction time. These newly formed bulky carbocations gradually succeeded SMS as the crucial reaction intermediate and catalyzed the methanol reaction in a more efficient way in the following reaction period. As shown in the inset in Figure 4, the great improvement of propene formation after feeding methanol for  $\sim 10$  min signified that the indirect pathway, methanol reaction proceeding with phenyl or alkenyl as intermediates, has almost taken over the direct pathways mediated with SMS. With the accumulation of HCP species on the catalyst surface, the indirect reaction mode, autocatalytic methanol conversion would dominate in the following reaction period and present a highly efficient reaction.

In summary, a complete prospect of methanol conversion over HSAPO-34 during the induction period has been presented based on the spectroscopy studies. The correlation establishment between DME/methanol and SMS suggested that the initial C–C bond was formed via the direct reaction of surface C1 reactant, DME/methanol, and the C1 intermediate, SMS. **Once initial olefins were formed, they would be transformed to bulky hydrocarbons, such as aromatics, oligomerized olefins and reactive carbocations,** which can trigger the efficient methanol reaction via the indirect route. With the evolution of the reaction mode from direct mechanism to indirect mechanism, alkenyl or/and phenyl carbocations will take over SMS as the intermediates for the assembly of C–C bond from methanol. From the SMS-mediated initial C–C bond generation to the MTO reaction proceeding with indirect pathway of autocatalysis cycle, a deep

understanding has been established for the methanol conversion during the induction period of MTO process over HSAPO-34.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.8b02385.

Experimental section, characterization data, and additional results (PDF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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