

Coke Formation and Carbon Atom Economy of Methanol-to-Olefins Reaction

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The methanol-to-olefins (MTO) process is becoming the most important non-petrochemical route for the production of light olefins from coal or natural gas. Maximizing the generation of the target products, ethene and propene, and minimizing the production of byproducts and coke, are major considerations in the efficient utilization of the carbon resource of methanol. In the present work, the heterogeneous catalytic conversion of methanol was evaluated by performing simultaneous measurements of the volatile products generated in the gas phase and the confined coke deposition in the catalyst phase. Real-time and complete reaction profiles were plotted to allow the com-

parison of carbon atom economy of methanol conversion over the catalyst SAPO-34 at varied reaction temperatures. The difference in carbon atom economy was closely related with the coke formation in the SAPO-34 catalyst. The confined coke compounds were determined. A new type of confined organics was found, and these accounted for the quick deactivation and low carbon atom economy under low-reaction-temperature conditions. Based on the carbon atom economy evaluation and coke species determination, optimized operating conditions for the MTO process are suggested; these conditions guarantee high conversion efficiency of methanol.

Introduction

Since the industrial revolution, there has been a large dependency on fossil resources and energy. Nowadays, the supply of fossil resources is becoming scarce; this scarcity requires efficient and cautious usage of them. Making the best of the few natural resources is the first consideration of chemical industry. The light olefins, ethene and propene, are crucial components in the petrochemical industry and are mostly used to produce plastics, fibers, and other chemicals. The main commercial technique for light-olefin production is steam-cracking of naphtha; this requires high reaction temperatures and consumes large amounts of oil resources and energy.^[1] Though some innovative technologies have been developed in terms of energy efficiency, it is still the primary energy-consuming process in the petrochemical industry. Alternative routes for light olefin production have been developed, among which the methanol-to-olefins process (MTO) is becoming the most important non-petrochemical route for light-olefin production from coal or natural gas.^[2] In August 2010, the World's first successful commercial application of the MTO process (dimethyl ether/methanol-to-olefin, DMTO), with a production capacity of 600 000 ton of light olefins per annum, was reported.^[3] Through the usage of a very effective catalyst, a silicoaluminophosphate zeolite with 8-membered ring windows and a chabazite cage (SAPO-34), the conversion of methanol (MeOH) had an extremely high olefin selectivity under mild reaction conditions.^[4]

The successful application of the MTO process requires the highly efficient conversion of methanol to the desired products with no or very little byproduct generation under set reaction conditions. To measure the potential of a methanol conversion route, one needs to compare the conversion efficiency under

varied reaction conditions and the cost associated with unrecoverable carbon resources. Atom economy,^[5] an important concept of green chemistry philosophy, is introduced in this study, and methanol conversion efficiency is taken into account in terms of carbon atom economy. According to the definition of atom economy, carbon atom economy of methanol conversion in the present work is described by Equation (1):

$$\text{C atom economy (\%)} = \frac{\text{C atoms of desired products}}{\text{C atoms of methanol}} \quad (1)$$

Usually, catalytic performances tested by continuous flow reactions and analyzed by using online gas chromatography can give a detailed distribution of effluents.^[2] Methanol conversion and the selectivity of volatile products are determined, but the carbon resource trapped in the catalyst phase as confined coke species are not considered in this way. SAPO-34 possesses a narrow 8-ring pore opening and a large supercage, which can accommodate a relatively large volume of coke materials, so the evaluation of carbon atom economy of methanol con-

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version needs a more complete measurement of methanol transformation with the consideration of coke formation. In previous studies, beside general catalytic tests, multi-techniques, such as in situ XRD, Raman, UV/Vis, and NMR spectroscopy and microbalance were employed to investigate the heterogeneous catalysis of methanol conversion.^[6] Comprehensive information about the volatile and catalyst phases in methanol conversion is helpful in understanding the coke deposition and related catalytic performances. Chen and coworkers published a series of work about catalyst deactivation in methanol conversion by the usage of a tapered element oscillation microbalance (TEOM).^[7] This technique was also employed in our work for the investigation of methanol conversion over catalyst with coke deposition under the working conditions. In the present work, carbon resource transformation in the conversion of methanol was determined by performing online gas chromatography in combination with catalyst mass change evaluation using a time-resolved microbalance. A complete overview of methanol conversion was plotted for more precise carbon atom economy evaluation and comparison of different reaction temperatures, revealing that coke formation using SAPO-34 had a large impact on the methanol conversion efficiency.

Coke generation, one of the most important issues of the MTO reaction, has been intensively studied in the last two decades.^[8] Coke species in the MTO process are responsible for catalyst deactivation by poisoning active sites and blocking pores.^[9] Due to the narrow pore opening and large supercage (ca. 1 nm), methanol conversion over SAPO-34 is characterized by very quick coke formation and deposition.^[6,9] In the industrial MTO process, the fluidized-bed technique is employed to maintain catalyst reactivity within the reaction–regeneration cycle.^[3] The removal of confined coke species implies the consumption of carbon resources of methanol and CO₂ emission. Prevention of coke formation is of great importance for the efficient utilization of the carbon resource of methanol.^[8] Conversely, mechanism studies have proved that large coke fragments stem from the transformation of the confined aromatic precursor and some of these confined coke species, such as polymethylbenzene and their protonated C₄⁺ cations, behave as the important reaction centre for C–C bond assembly from the C1 reactant, methanol.^[9,10] To understand methanol conversion and catalyst deactivation, it is essential to know the main features of coke, such as composition, mode of formation, location, as well as how coke affects the catalytic properties.^[8–10] A detailed investigation of confined coke in methanol conversion was performed under the fluidized-bed reaction conditions. Coke species that formed at varied temperatures were determined. The observations presented in this study identified polycyclic aromatics as the main coke species at reaction temperatures higher than 350 °C and showed an exception to this trend at low reaction temperatures. A new type of confined coke species formed abundantly as the retained compounds in the nanocage of SAPO-34 and caused quick deactivation at low reaction temperatures. Understanding the coke species evolution with temperature is important for the prevention of coke formation and is also required in operating a

MTO process under optimized conditions with high carbon atom economy.

Results and Discussion

Coke formation and evaluation of carbon atom economy

Generally, the catalytic performance of the MTO reaction is described in terms of methanol conversion, light-olefin selectivity, and catalyst life (time for breakthrough of methanol). The measurement of coke, coke species and coke amount determination, is usually performed offline after completion of the reaction.^[8] In heterogeneous catalysis, the concentration of acidity and the available surface of the catalyst are essential for the reaction performed on the surface of the solid-acid catalyst.^[11] The coverage of the catalyst surface by coke deposition would give rise to variable catalytic performance with time-on-stream.^[7] Real-time observation of coke deposition will be of great significance to interpret how coke affects methanol conversion. In this section, catalytic testing of the heterogeneous reaction of methanol and the measurement of catalyst mass change were performed under working conditions to observe the product generation in the gas phase and coke deposition in the catalyst phase at the same time. Based on the calculation of the effluent rate of volatile hydrocarbons and unconverted reactants (methanol or dimethyl ether) in the gas phase and time-resolved coke formation rate in the catalyst phase, a complete reaction profile was displayed for the evaluation of the conversion efficiency of the carbon resource in the conversion of methanol catalyzed by SAPO-34.

Methanol conversion over SAPO-34

Methanol conversion over SAPO-34 was performed by using a setup that included a microscale fixed-bed reactor equipped with an online gas chromatography for product analysis and a sensitive TEOM for the testing of simultaneous coke formation on the catalyst surface.^[7] Within the temperature range of 250–500 °C, the methanol conversion and mass increase in the catalyst phase with time-on-stream are presented in Figure 1.

The comparison of methanol conversion at different temperatures indicated that the lifetime of the SAPO-34 catalyst varied with the reaction temperature (Figure 1 a), as was observed in the normal continuous-flow transformation of methanol.^[12] Within the temperature range of 350–500 °C, initial methanol conversion was 100% and the high conversion value was maintained for more than 200 min at 400 and 450 °C and nearly 60 min at 350 and 500 °C. For the reaction performed at 300 °C, the conversion of methanol was characteristic of the induction period reaction and very quick deactivation.^[10e,12,13] Very low initial conversion, especially the extremely low conversion at 300 °C, showed the low conversion efficiency over the fresh catalyst in the induction period. Prolonging the reaction time increased the conversion to a maximum value, which then declined. Very low conversion occurred at 250 °C with a very slight increase in methanol conversion from the initial period to 100 min time-on-stream.

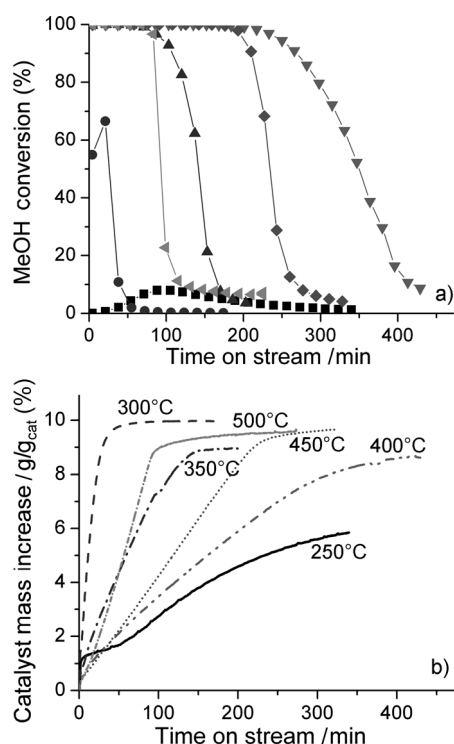
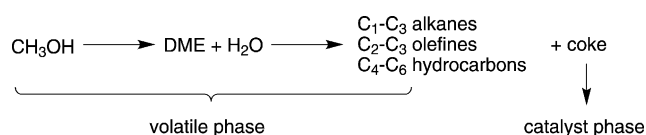


Figure 1. a) Methanol conversion (■ 250, ● 300, ▲ 350, ▼ 400, ◆ 450, and ◀ 500 °C) and b) real-time catalyst mass increase observation.

Mass increase in the catalyst phase, representing the occurrence of coke formation, was observed as soon as methanol was fed into the reactor and contacted with the catalyst (Figure 1b). Even for the reactions performed at the low temperatures of 250 and 300 °C, with obvious induction periods and very low conversions, the catalyst gained weight from the beginning of the reaction. With the extension of time-on-stream, the reactions performed at 300 °C and the high temperature of 500 °C presented very sharp mass increases in the catalyst phase with time-on-stream, whereas at 400 and 450 °C, long catalyst life was exhibited along with relatively mild coke deposition. A slight catalyst mass increase occurred at 250 °C together with very inefficient methanol conversion. Notably, under these conditions, most of the methanol was transformed to dimethyl ether (DME) in the gas phase and higher hydrocarbon products had a low yield, whereas the amount of confined organics still increased with time-on-stream, implying coke formation in the catalyst phase. From the results of effluent distribution determined with online GC and coke formation measured with the microbalance, it was concluded that the formation and accumulation of confined coke species in the SAPO-34 catalyst differed from the reaction temperature of methanol conversion. Correspondingly, the conversion efficiency of methanol, which is closely related with coke formation, also varied with the time-on-stream and reaction temperature.

Carbon resource prospects during methanol conversion

Over the SAPO-34 catalyst, the carbon resource from the methanol feed was transformed into products in the volatile and catalyst phases (Scheme 1). The compounds in the volatile



Scheme 1. Heterogeneous catalytic conversion of methanol

phase were composed of ethene and propene (target products), C₁–C₃ alkanes (byproducts), C₄–C₆ hydrocarbons (byproducts), DME (intermediate product), and unconverted MeOH. In the catalyst phase, coke formed and remained. Light olefins are target products of the MTO process and can be generated over the SAPO-34 catalyst with high selectivity.^[4] C₄ products and hydrocarbon products (higher than C₄) among the effluent products (almost C₄–C₆ alkenes) could be separated from other products and recycled to the reactor for a further transformation to enhance the selectivity of light olefins. Carbon atom economy of MTO would profit from the selectivity increase of light olefins with the usage of an excellent catalyst under the appropriate reaction conditions and the recovery and reuse of the C₄⁺ hydrocarbons at the same time.^[5] Coke formation costs the carbon resource from methanol, and C₁–C₃ alkanes are also less value-added products. Combining the online analysis of volatile products and real-time coke deposition measurement, the heterogeneously catalyzed transformation and utilization of carbon resource from methanol was plotted in terms of the formation or effluent rate of each component containing the carbon atoms from methanol (Figure 2). Considering the difference of catalyst life at varied reaction temperatures, the plots of carbon resource distribution are displayed in the reaction period with 0–120 min time-on-stream.

Methanol conversion at temperatures higher than 350 °C presented very efficient light-olefin production. Most of the carbon resources from methanol were transformed to the target products, ethene and propene. The propene-to-ethene ratio and the generation of recoverable products, C₄–C₆ hydrocarbons, differed with reaction temperature. Carbon resource loss due to coke formation and light alkane generation also varied with the reaction temperature. For the reactions performed at 400 and 450 °C, methanol conversion was 100% in the reaction period from the initial conversion to 120 min time-on-stream. For the reactions performed at 350 and 500 °C, initial conversion was 100%, but catalyst deactivation occurred after 50 and 60 min time-on-stream, respectively; MeOH and DME appeared at prolonged reaction times. In industrial MTO processes, the reaction-regeneration technique is required for keeping the high reactivity of the SAPO-34 catalyst. Compared to the catalytic performances at 400 and 450 °C, reaction at 500 °C also consumed more carbon resource with relatively severe coke deposition. At the reaction stage with high reactivity for light-olefin production (0–60 min time-on-stream), about 6–7% carbon atoms from methanol are retained on the catalyst as confined coke species. This is higher than the average value of 3–4% at 400 or 450 °C. Besides the high conversion and low carbon cost in coke, from the point of byproduct usage, methanol conversion at 400 and 450 °C

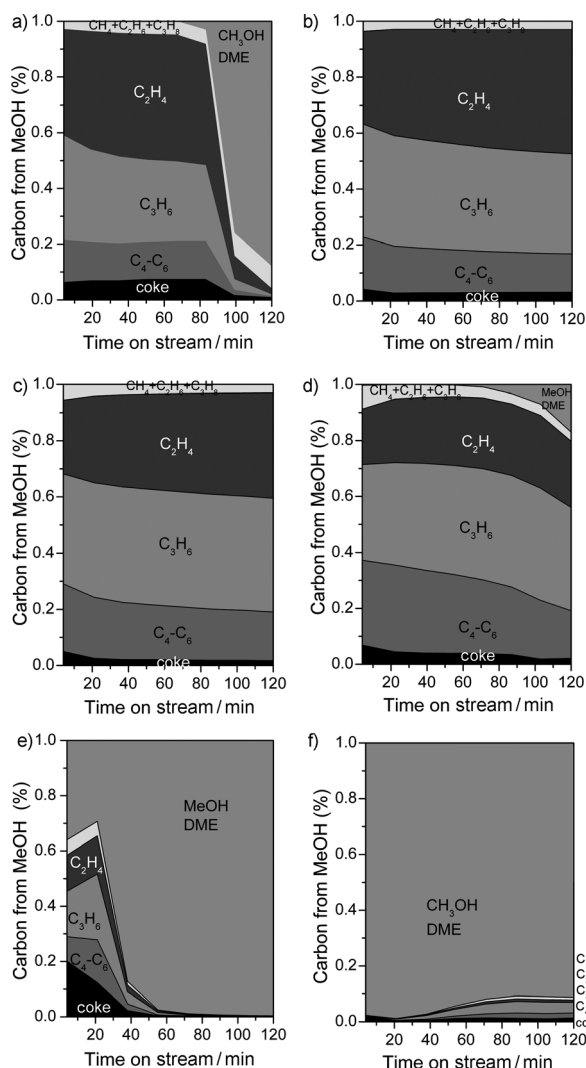


Figure 2. Reaction profiles of heterogeneous methanol conversion at a) 500, b) 450, c) 400, d) 350, e) 300, and f) 250 °C.

generated relatively more C_4 – C_6 hydrocarbons compared to 500 °C, which could be recovered for further transformation.

Methanol conversion at 300 °C presented low efficiency from the beginning of the reaction. After a slight increase in methanol conversion, quick deactivation occurred, which left a large proportion of carbon resource as unconverted MeOH and DME. Contrary to the low methanol conversion and light-olefin generation, the predominant coke formation is at 300 °C. The carbon resource loss in the confined coke species was about 20% of that from methanol feed at 4 min time-on-stream. With the occurrence of quick deactivation, the percentage of carbon atoms, both as volatile products and coke species, declined and complete deactivation of the catalyst occurred after 70 min time-on-stream. When the reaction was performed at the lowered reaction temperature of 250 °C, almost no conversion was observed. A very slight increase in product generation and coke deposition with time-on-stream indicates that following contact with the SAPO-34 catalyst for 120 min, the catalyst does not convert methanol to light olefin anymore and is still

not a working catalyst.^[13] The long induction period implies that the reaction at 250 °C is totally non-applicable for the operation of MTO process.

Carbon atom economy of methanol conversion

Carbon atom economy of methanol conversion with ethene and propene as the target products was evaluated and is demonstrated in Figure 3. Recycling of C_4 products and hydrocarbons higher than C_4 (C_4^+) for further transformation was con-

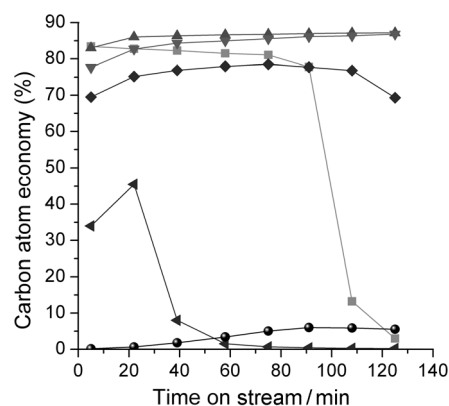


Figure 3. Carbon atom economy of methanol conversion at varied reaction temperatures (■ 500, ▲ 450, ▼ 400, ◆ 350, ◀ 300, and ● 250 °C).

sidered; C_4^+ alkenes account for about 85% of the C_4^+ hydrocarbon products. The catalytic cracking of these higher alkenes was evaluated, and the yield of ethene and propene from the transformation of butenes was about 60% (see the Supporting Information, Table S1). Carbon atom economy was calculated based on Equation (2).

$$C \text{ atom economy (\%)} = \frac{C \text{ atoms of } (C_2H_4 + C_3H_6)}{C \text{ atoms of } CH_3OH \text{ feed}} \quad (2)$$

where C_2H_4 and C_3H_6 originate from the conversion of MeOH and recycled C_4^+ .

The carbon atom economy was very poor for methanol conversion at low reaction temperatures, such as 300 °C, which stems from the low conversion efficiency in the gas phase and severe coke accommodation on the catalyst. In the methanol conversion performed at a high temperature (500 °C), besides the formation of light olefins, a relatively large amount of coke species were also generated, which are usually more H-deficient ($H/C < 1$) than the reactant (MeOH, $H/C = 2$) and olefin products ($H/C = 2$).^[8] Correspondingly, light alkanes ($H/C > 2$) appeared among the products for hydrogen balance. The loss of carbon resources in coke and light alkanes formation reduced the carbon atom economy at 500 °C. Slight coke deposition and less byproduct generation were responsible for the relatively high methanol conversion efficiency under the mild reaction conditions with reaction temperatures of 400 and 450 °C. The predominant generation of C_4^+ hydrocarbons under these conditions, which can be recycled and reused in

light-olefin production, was also very helpful for the improvement of carbon atom economy. Interestingly, the carbon atom economy of methanol conversion improved with time-on-stream under the optimized reaction conditions at 400 and 450 °C in the displayed reaction period of 0–120 min. This implies that SAPO-34 with a fresh surface is not the most efficient catalyst for light-olefin production from methanol. The confinement of some coke species, which behave as the active reaction center according to the mechanism of hydrocarbon pool, will transfer the fresh catalyst to a very effective working catalyst for methanol conversion.^[9] Coke deposition during methanol conversion also modifies the acid-site concentration of SAPO-34 and suppresses some side reactions, such as the H-transfer reaction.^[13] The increase of carbon atom economy with time-on-stream at 400 and 450 °C benefits from the reduction in the rate of formation of byproducts, coke and light alkanes, and the enhancement in the rate of formation of target products with prolonged reaction time.

Coke-species determination

During methanol conversion, coke-species formation and deposition in the cage or channel of SAPO-34 have an important impact on the conversion of methanol. In acid catalysis, coke deposition causes active-site coverage or mass-transfer difficulty of reactants and both will depress the transformation.^[7] In the present study, the reaction evidences of the initial methanol conversion and the catalyst deactivation imply that a low-temperature reaction with poor carbon atom economy may differ from the conversion at high temperatures in the build-up of the confined active reaction centers for methanol conversion at the beginning of the reaction and the deposition of coke during the deactivation period;^[9,10] therefore, the coke species formed at different temperatures was determined.

Studies have reported the catalytic performances and coke formation in SAPO-34-catalyzed methanol conversion on the basis of the reactions performed in the fixed-bed reactor. Fixed-bed reactions sometimes encounter the radial and axial gradients of temperature, gas phase composition, and carbon deposition on the catalyst.^[14] The analysis of coke species derived from the locally overheated catalyst bed, caused by the exothermal effect of methanol conversion or “burning-cigar”-like catalyst bed,^[14d] was somewhat unreliable or unrepresentative. For a precise determination of the coke species trapped in the catalyst of SAPO-34, methanol conversion was performed in a microscale fluidized-bed reactor to achieve spatial uniformity of the catalytic reaction and coke deposition at varied reaction temperatures.

The fluidized-bed conversion of methanol over SAPO-34 catalyst was investigated in the temperature range of 300–450 °C. In each test, when methanol was fed into the fluidized-bed reactor, no obvious temperature increase of the catalyst bed was detected. The conversion and product selectivity (see the Supporting Information, Figures S1 and S2) presented a similar trend as observed in the fixed-bed transformation of methanol.^[12] The lifetime of the SAPO-34 catalyst also varied with the reaction temperature. Methanol conversion performed within

the temperature range 375–450 °C presented very high initial methanol conversion, and the high conversion value was maintained for more than 200 min, whereas for the reactions performed at 300, 325, and 350 °C, methanol conversion was low. The conversion at 300 and 325 °C presented the character of the induction period at the initial reaction stage with very low methanol conversion efficiency and quick deactivation prolonging the reaction time. These observations are very close to the catalytic performances of methanol conversion, which was performed in the microscale reaction element of TEOM setup at varied temperatures. Fluidized-bed operation did not alter the coke species, but guaranteed the space uniformity of the coke deposition.

Coke species determination at 375–450 °C

Following reaction completion, the completely deactivated catalysts were analyzed by using the method introduced by Guisnet.^[8] Figure 4 compares the chromatograms of the extracted hydrocarbons from the deactivated catalyst after reaction at

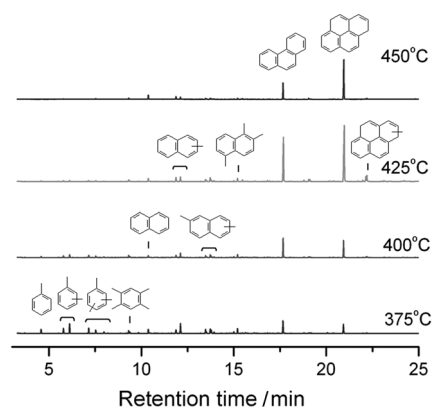


Figure 4. Coke species formed after methanol conversion within the temperature range 375–450 °C.

375–450 °C. Among the confined organic species generated at 375 °C, methyl-substituted benzene and naphthalenes, and polycyclic aromatics, such as phenanthrene and pyrene, were present. These polycyclic aromatic coke species intensified with an increase in reaction temperature and became the most important retained compounds after reaction at higher temperatures.^[9,12] Methylbenzene hydrocarbons, especially polymethyl benzenes, were very scarce in the deactivated catalyst. This is in line with the aging of trapped methyl benzenes to polycyclic aromatics.^[8,9] Catalyst deactivation of methanol conversion at relatively high reaction temperatures results from generation of large aromatics, which causes acid-site coverage and channel or cage blockage of the catalyst.^[9d,f]

Coke species determination at 300–350 °C

The retained compounds of the deactivated catalyst were also analyzed after methanol conversion at 300–350 °C (Figure 5). After reaction at 350 °C, as was observed in the deactivated catalyst after reaction at 375–450 °C, confined organics, mainly

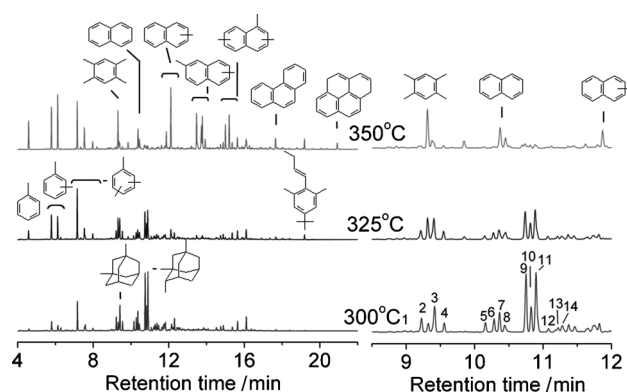


Figure 5. Coke species formed after methanol conversion within the temperature range 300–350 °C. The numbers 1–14 correspond to the entries in Table 1.

composed of aromatics hydrocarbons, were observed. Methyl-substituted benzenes and naphthalenes were present in the chromatograms as the main coke species and polycyclic aromatics, phenanthrene, and pyrene also appeared with relatively low intensity compared to the confined coke species formed at high temperature. The deactivation of SAPO-34 in the methanol conversion at 350 °C mainly results from the formation of aromatic coke species, especially polycyclic aromatics, as for the reactions at 375–450 °C.^[8] A noteworthy and surprise observation is that species other than aromatics were detected among the retained materials of the catalysts after reaction at 300 and 325 °C. Especially in the catalyst deactivated at 300 °C, some very strong peaks appeared at retention times of 9–13 min. These major peaks were identified as alkyl-adamantanes by the library of NIST08 and the reference literature.^[15] The identification of the marked peaks is detailed in Table 1. Among the confined compounds, methyl-substituted benzenes, including methylbenzene, dimethylbenzene, trimethylbenzene, and tetramethylbenzene, were detected, whereas adamantane hydrocarbons, especially dimethyl- and trimethyladamantanes, dominated. In the early work of Arstad and Kolboe, adamantane hydrocarbons were found as part of the trapped species in the catalyst at the beginning of methanol conversion,^[10b] but in the study of Bleken and coworkers,^[12] retained compounds in the catalyst of SAPO-34 after reaction at

300 °C were composed of aromatic hydrocarbons, such as methyl benzenes or methyl naphthalenes, and no adamantane derivatives were observed. In our present work, adamantane hydrocarbons were detected in abundance and became the most significant materials among the coke species. The absence of naphthalenes and polycyclic aromatics in the deactivated catalyst after reaction at 300 °C implies that the quick deactivation and low conversion efficiency at low temperature is very probably related to the generation and occlusion of this new kind of non-aromatic coke species in methanol conversion. The formation of adamantanes, a type of hydrocarbon with three-dimensional and diamondoid structure^[16] and being newly-found as confined organic species in the catalyst in the present work, will be investigated in our future study of methanol conversion at low temperature.

Conclusions

Combined measurements of product generation in the volatile phase and coke deposition in the catalyst phase provided a complete reaction profile of heterogeneous catalysis of methanol conversion over the catalyst SAPO-34. Carbon atom economy gave the highest value under mild reaction conditions at the reaction temperature around 450 °C due to the high methanol conversion efficiency for light-olefin production and the low coke or less byproducts generation. Quick deactivation with abundant coke formation makes the low temperature reaction not applicable for methanol conversion. Relatively severe coke deposition and predominant light-alkane generation also depressed the carbon atom economy of the high temperature reaction (500 °C). Detailed analysis of confined coke compounds indicated that the coke species varied with reaction temperature. The formation of polycyclic aromatic hydrocarbons as the confined coke species was responsible for the deactivation of methanol conversion at temperatures higher than 350 °C. A new type of coke species, adamantane hydrocarbons, was detected among the confined organics after methanol conversion at low temperature. The formation of these cyclic and saturated hydrocarbons and their accommodation in the supercage of SAPO-34 accounted for the quick deactivation and poor carbon atom economy under the condition of low reaction temperature.

Experimental Section

Reaction plot of methanol conversion over SAPO-34

SAPO-34 was synthesized using the literature procedure^[17] with (Al+P)/Si = 16. The experimental setup of methanol conversion, including a fixed-bed reactor and a sensitive microbalance (TEOM series 1500, Rupprecht & Patashnick), was designed for continuous-flow methanol conversion performed at atmospheric pressure. For each test, a catalyst sample (100–150 mg, 40–60 mesh) was loaded into the reactor. The catalyst was heated to 500 °C and maintained for 1 h in helium flow before the reaction and then the temperature was adjusted to the reaction temperature ranging from 250–500 °C. Methanol was fed by passing the helium gas through a saturator containing methanol at 33 °C, which gave a

Table 1. GC/MS identification of adamantane hydrocarbons among the retained compounds in the SAPO-34 catalysts.

Entry	Compounds	Abbreviation	Formula
1	adamantane	A	C ₁₀ H ₁₆
2	1-methyladamantane	1-MA	C ₁₁ H ₁₈
3	1,3-dimethyladamantane	1,3-DMA	C ₁₂ H ₂₀
4	1,3,5-trimethyladamantane	1,3,5-TMA	C ₁₃ H ₂₂
5	2-methyladamantane	2-MA	C ₁₁ H ₁₈
6	1,4-dimethyladamantane, cis-	1,4-DMA, cis-	C ₁₂ H ₂₀
7	1,4-dimethyladamantane, trans-	1,4-DMA, trans-	C ₁₂ H ₂₀
8	1,3,6-trimethyladamantane	1,3,6-TMA	C ₁₃ H ₂₂
9	1,2-dimethyladamantane	1,2-DMA	C ₁₂ H ₂₀
10	1,3,4-trimethyladamantane, cis-	1,3,4-TMA, cis-	C ₁₃ H ₂₂
11	1,3,4-trimethyladamantane, trans	1,3,4-TMA, trans-	C ₁₃ H ₂₂
12	1-ethyladamantane	1-EA	C ₁₂ H ₂₀
13	1-methyl-3-ethyladamantane	1-M-3-EA	C ₁₃ H ₂₂
14	1,3-dimethyl-5-ethyladamantane	1,3-DM-5-EA	C ₁₄ H ₂₄

weight hourly space velocity (WHSV) of 2.0 h^{-1} . Once methanol was fed into the reactor, the catalyst mass change was measured by using TEOM. The effluent was kept at about 180°C and analyzed online by using a gas chromatography (Varian 3800) equipped with a capillary column of Pora Plot Q-HT and a flame ionization detector (FID) detector.

In methanol conversion, the carbon resource from methanol was transformed to hydrocarbon products and coke species. When the conversion was lower than 100%, unconverted methanol or dimethyl ether appeared among the effluents. A complete reaction prospect of the transformation of carbon resource from methanol was plotted on the basis of the calculation of the time-resolved formation rate of coke, the formation rate of volatile hydrocarbons, and the effluent rate of methanol and dimethyl ether. Carbon resource in reactant and products, including volatile products and deposited coke, was measured on a CH_2 basis. Some definitions and calculations are summarized in the Supporting Information.

The catalytic test performed in the TEOM setup allowed the measurement of coke formation rate in real time. In combination with the GC analysis for volatile products, the carbon resources can be classified and ascribed to the target product, byproduct, coke, or unconverted methanol and dimethyl ether. With the normalization of the generation or effluent rate from each part, the complete carbon resource transformation of methanol with time on steam could be plotted.

Fluidized-bed catalytic test and coke species determination

The fluidized-bed catalyst was prepared by the spray-dry method and composed of SAPO-34^[17] and inert matrix. Before the test, the catalyst (10 g) was loaded in the reactor and pre-treated at 550°C in helium flow (30 mL min^{-1}) for 1 h and then the temperature was adjusted to the desired reaction temperature. By switching to a 4-port valve, the reactant (40% aqueous methanol) was pumped to a preheater, vaporized at 250°C and then entered the reactor through a distributor and contacted with the catalyst. All the effluents from the reactor were kept warm at about 180°C and analyzed online by gas chromatography (Varian 3800) fixed with a capillary column of Pora Plot Q-HT and a FID detector.

The determination of confined coke species followed the procedure of Guisnet.^[8] After the reaction, the catalyst was quickly cooled to room temperature and removed from the reactor. Part of the discharged catalyst was dissolved in HF solution and the organics retained in the catalyst were extracted with CH_2Cl_2 containing chlorobenzene as the internal standard. Analysis of the organic phase was performed by gas chromatography equipped with a HP-5 column, a FID detector and a mass selective detector (Agilent 7890/5975C).

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