Electronic Supplementary Information for

Generation of diamondoid hydrocarbons as confined compounds in SAPO-34 catalyst in the conversion of methanol

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Experimental

The fixed-bed reaction of MTO is usually accompanied by the radial and axial gradients of temperature, gas phase composition and as well as coke deposition on the catalyst.[1] For a spatial uniformity of the catalytic reaction and coke deposition, methanol conversion was carried out in a microscale fluidized-bed reactor. The fluidized-bed catalyst was prepared by spray-dry method and composed of SAPO-34 ((Al+P)/Si=16) and inert matrix. SAPO-34 was synthesized using standard procedures.[2] Before test, the catalyst was loaded in the reactor and pretreated at 550 °C in He flow for 1 h and then the temperature was adjusted to the desired temperature. By switching a 4-port valve, the reactant (40% methanol aqueous solution), which was vaporized in a preheater, entered the reactor through a distributor and contacted with the catalyst.

Coke analysis followed the method introduced by Guisnet and co-worker[3] using a gas chromatograph equipped with a FID detector and a mass sensitive detector (Agilent 7890A/5975C).

^{1}H-^{13}C CP/MAS NMR spectra were acquired on a Bruker AvanceIII 600 spectrometer using a 4 mm MAS probe at the resonance frequency of 150.9 MHz and a spinning rate of 8 kHz. The chemical shifts were referenced to adamantane with the upfield methine peak at 29.5 ppm.

UV-Vis measurements between 200 and 800 nm in the diffuse reflection mode were conducted with a Varian CARY5000 spectrometer.

For real time observation of catalyst deactivation, methanol conversions over SAPO-34, 18 and 35 were performed in an experimental setup including a Rupprecht & Patashnick TEOM 1500 mass analyzer.

Methanol conversion and product distribution at low reaction temperature

Methanol conversion over SAPO-34 catalyst at low reaction temperature, such as 300, 325 and 350 °C, presented induction period reaction and quick deactivation (Figure S1-1). Product distribution of methanol conversion is presented in Figure S1-2. Ethene, propene and butenes were the main products, among which, propene was the most important product with selectivity about 40%. In the induction period with the conversion increase from zero to the maximum, the reaction at 300 °C presented higher selectivity of ethene and propene than the reaction at 325 °C, while in the deactivation period with conversion decline to low value, compared with the reaction carried out at 325 and 350 °C, one can observe relatively low selectively of ethene and propene at 300 °C. It is worthy to note the predominant formation of methane at 300 °C, not only in the initial reaction stage but also during the deactivation period.

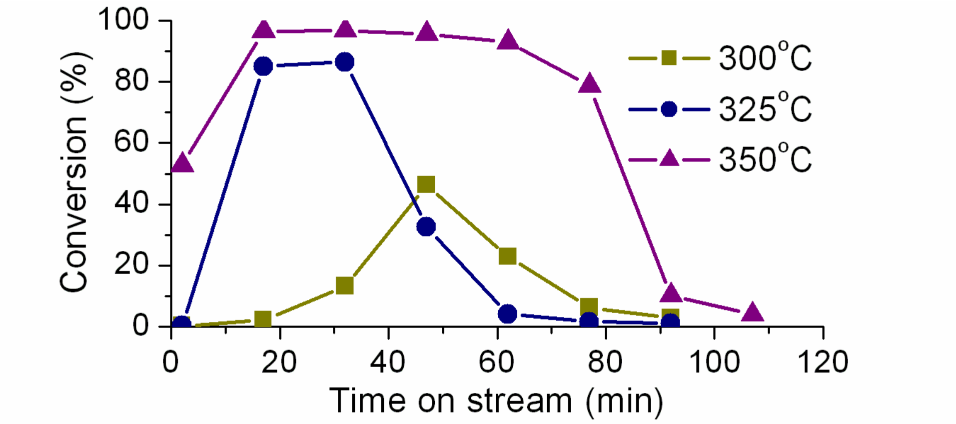


Figure S1-1. Methanol conversion over SAPO-34 catalyst in a microscale fluidized-bed reactor at 300, 325 and 350 °C.

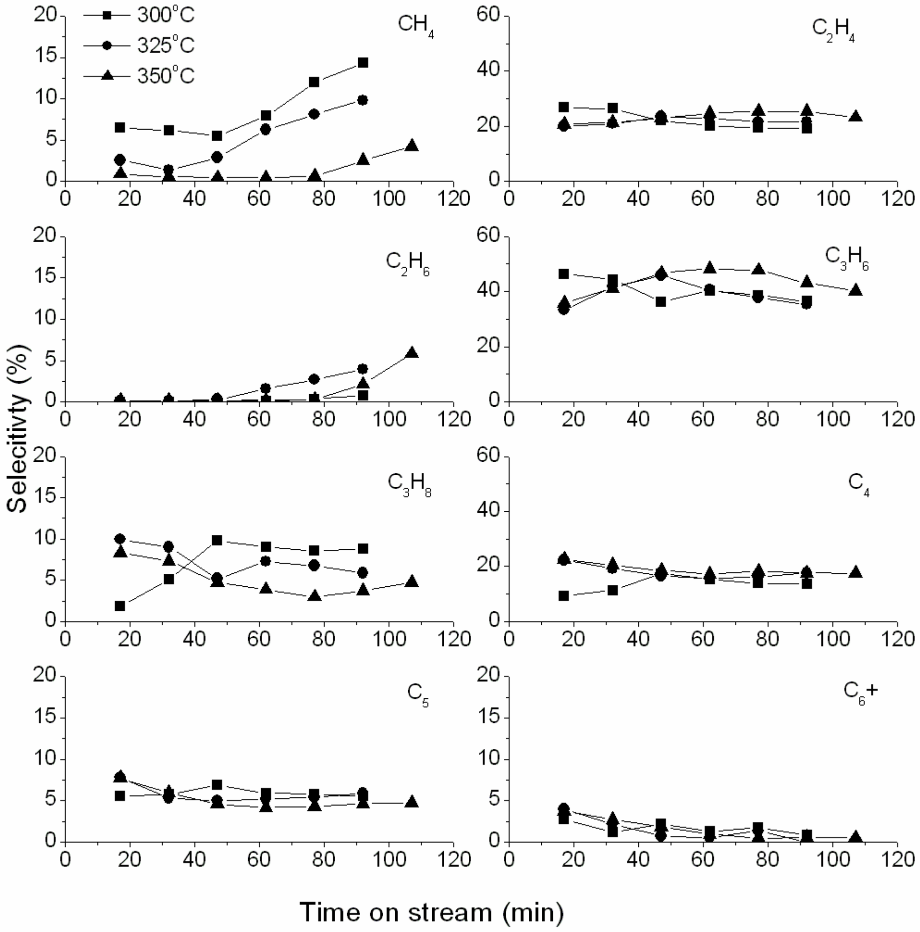


Figure S1-2. Product selectivity of methanol conversion at 300, 325 and 350 ^{o}C carried out in a microscale fluidized-bed reactor

Coke species identification

After methanol conversion at 300, 325 and 350 °C, the deactivated catalyst was dissolved in HF solution and the confined organics was extracted with CH_2Cl_2. The trapped organics were analyzed with GC-MS and the spectra are compared in Figure S2. When the reaction was carried out at 350 °C, polymethylbenzenes and methyl-substituted naphthalenes were more dominant and polycyclic aromatics, phenatherene and pyrene, can also be observed among the trapped coke species in low intensity. A surprise observation is that at 300 and 325 °C, some new coke species were detected among the extracted organics, especially at 300 °C, their intensity was much higher than aromatics species. By the library of NIST08 and reference literature,[4] they were identified as adamantane derivatives and the detailed identification of the marked peak is listed in Table S1.

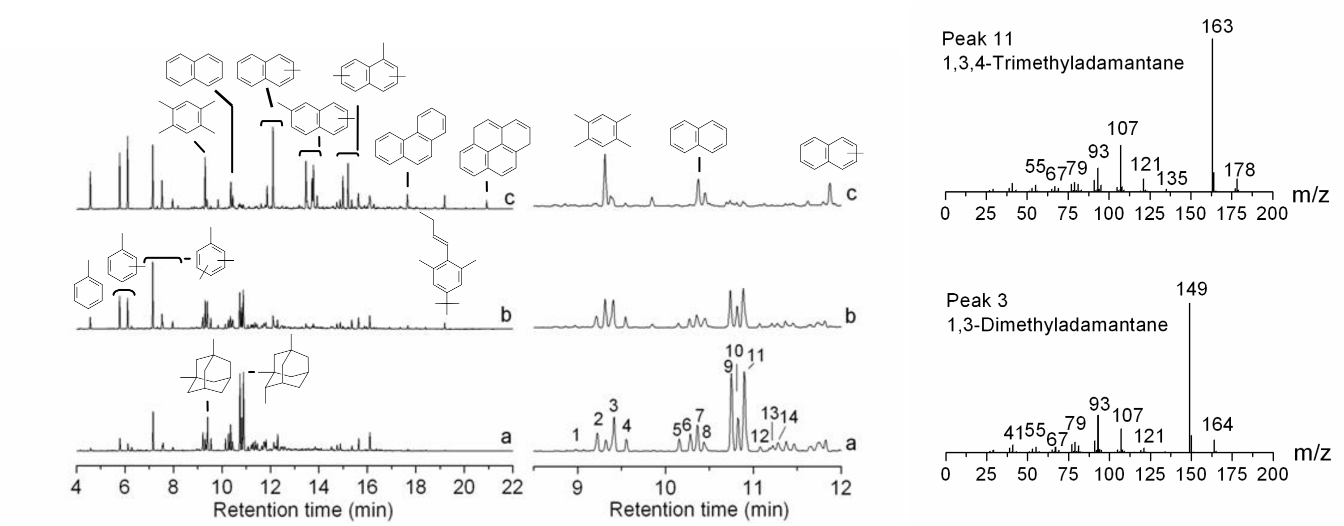


Figure S2 GC-MS analyses of retained materials in the completely deactivated catalysts after reaction at 300 (a), 325(b), and 350 °C (c).

Table S1 GC-MS identification of adamantane hydrocarbons among the retained compounds in the SAPO-34 catalysts

No	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	$C_{14}H_{24}$

^{1}H-^{13}C CP/MAS NMR and UV-Vis studies

The ^{1}H-^{13}C CP/MAS NMR and UV-Vis studies of the deactivated catalysts give distinct results according to the reaction temperature (Figure S3). After methanol conversion at 350 °C, the ^{13}C signals at 23, 127 and 136 ppm in the spectrum indicated the presence of alkylated aromatics, such as methylbenzenes, in the SAPO-34 catalyst. In the spectra of the catalysts deactivated at 325 and 300 °C, the intensity of the signals at 127 and 136 ppm in the aromatic region was low, especially these two signals almost disappeared in the spectrum recorded after the reaction at 300 °C. At the same time, the occurrence of the signals at 43, 38, 30 and 16 ppm in the region of alkyl groups implied that at relatively low reaction temperature, the coke species, different from aromatics, formed and retained in the catalyst.[5] Combining the GC-MS analysis, the resonance peaks at 30, 38 and 43 ppm in the ^{1}H-^{13}C CP/MAS NMR spectra were assigned to the carbon atoms from adamantane ring (α or γ-carbon (CH), β or δ carbon (CH2) and β carbon with neighbouring methyl substitution) and the signals at 16 ppm accounted for the carbon atoms from methyl substituting groups.[5c] Their intensity variation with reaction temperature (Figure 1d) demonstrated that more aromatics were generated at relatively high temperature and low-temperature reaction favored the generation of methyladamantane hydrocarbons as the trapped species. UV-Vis spectroscopy possesses a high sensitivity for the compounds with conjugated bonds, such as aromatics and oligomer hydrocarbons. In Figure S3, the band at 230 nm was assigned to the dienes and the bands at 250-280 nm stemmed from the absorbance of alkylaromatics. Noting that the absorbances at 475 and 510 nm, attributed to polycyclic aromatics and responsible for the colouration of the catalysts with coke deposition at 350 and 325 °C, were almost invisible in the spectrum of the deactivated catalyst after reaction at 300 °C.[6] The band around 400 nm, due to the absorbance of methyl-substituted benzenium cations, is also very weak for the deactivated catalyst at 300 °C. [6c]

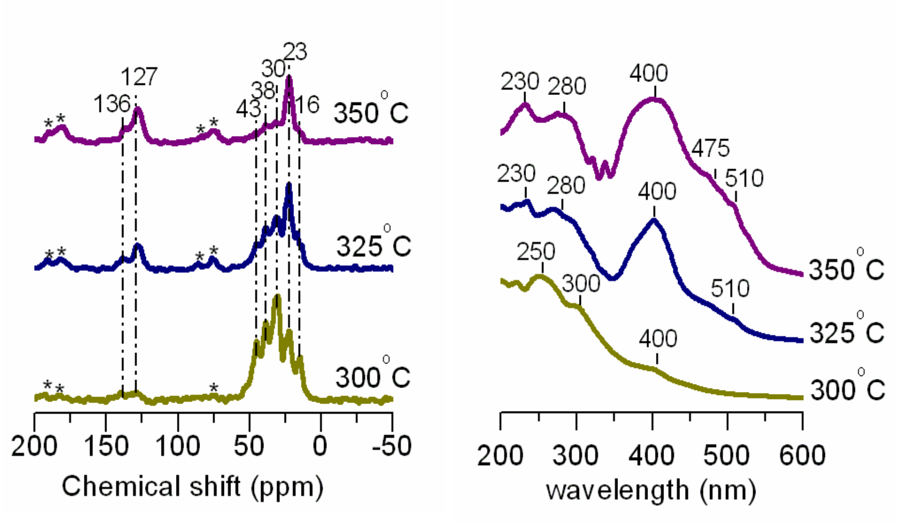


Figure S3. ^{1}H-^{13}C CP/MAS NMR (left) and UV-Vis (right) spectra of SAPO-34 catalysts after MeOH conversion at 300, 325 and 350 °C

Reactivity of confined compounds

After a continuous-flow reaction of ^{12}C-methanol over SAPO-34 for 0.5 h, a ^{13}C-methanol injection was conducted upon the catalyst. The reaction was then stopped and the catalyst was cooled very quickly. The discharged catalyst was dissolved in HF solution and the confined coke species was extracted with CH_2Cl_2 solution and analyzed by GC-MS. The mass spectra of the confined compounds (TetraMB, PMB, DMA and TMA) with possible isotopic distribution were given in Figure S4b and compared with that from ordinary methanol conversion (Figure S4a). In MTO reaction, polymethylbenzenes were supposed to be the reaction center which methanol was added to and ethene and propene could be split off from. In the present study, the reactivity of the retained materials was compared in term of the incorporation of ^{13}C-atoms from ^{13}C-CH_3OH into the previously deposited compounds formed in the conversion of ^{12}C-methanol.

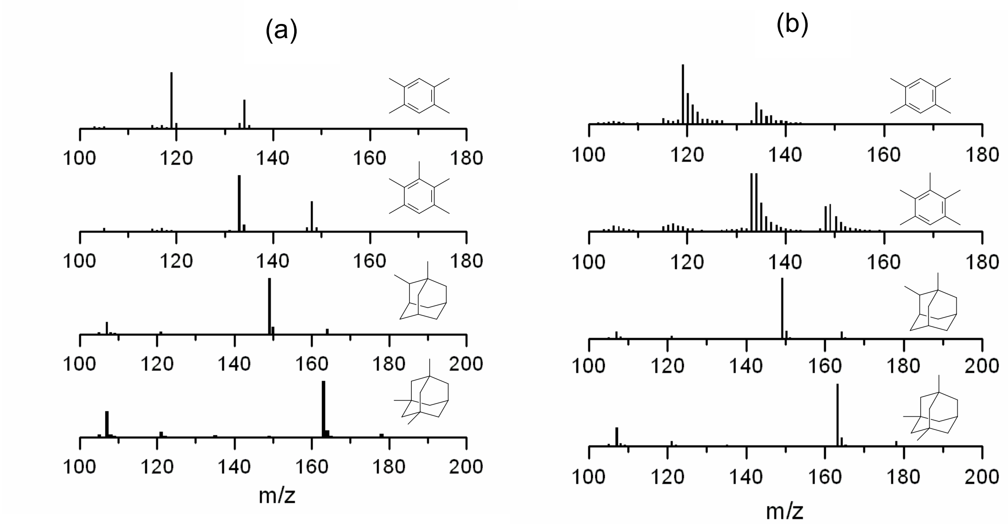


Figure S4 Mass spectra of the confined molecules, TetraMB, PMB, DMA and TMA retained in SAPO-34 catalyst

(a) after reaction in a continuous flow of ^{12}C-methanol for 0.5 h

(b) after reaction in a continuous flow of ^{12}C-methanol for 0.5 h and then upon which ^{13}C-methanol (3μl) was injected

Methanol conversion under the condition of temperature programmed increase: confined organics evolution

Besides the study of methanol conversion over SAPO-34 catalyst at 300 °C, methanol conversion under the condition of a reaction temperature programmed increase (250-400 °C) was also performed in a microscale fluidized-bed reactor and the deposited coke species formed during the reaction at different temperature range was analyzed (See Figure 5-1 and 5-2). In the temperature range of 300-350 °C, methylbenzenes and methyladamantanes were the main coke materials confined in the catalyst. With the adamantane hydrocarbons formation (300-350 °C), the conversion declined and catalyst deactivation occurred. It was interesting to find that these adamantane hydrocarbons were transformed to methylnaphthalenes and polycyclic aromatics at higher temperature range, such as 350-400 °C. The formation of aromatics coke species at enhanced temperature corresponded to the recovered methanol conversion at 350-400 °C.

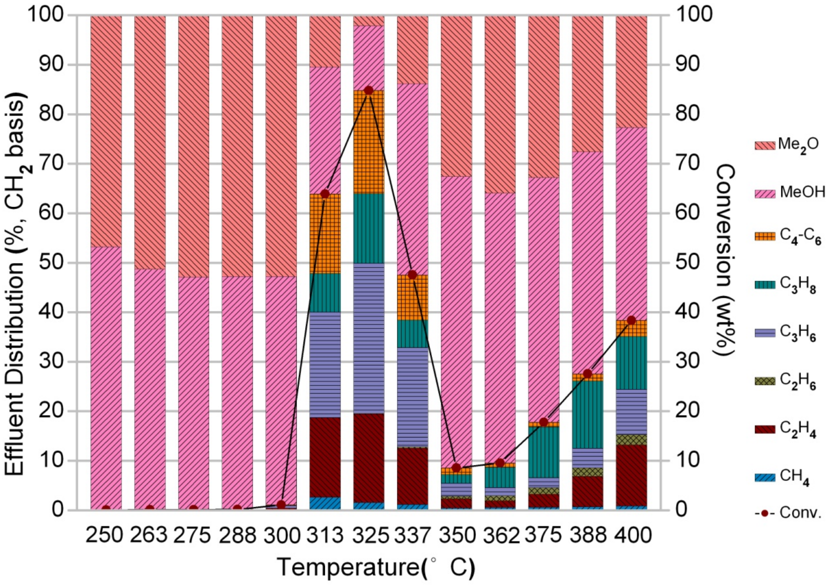


Figure 5-1 Effluent distribution of fluidized-bed methanol conversion under the condition of programmed increase of temperature

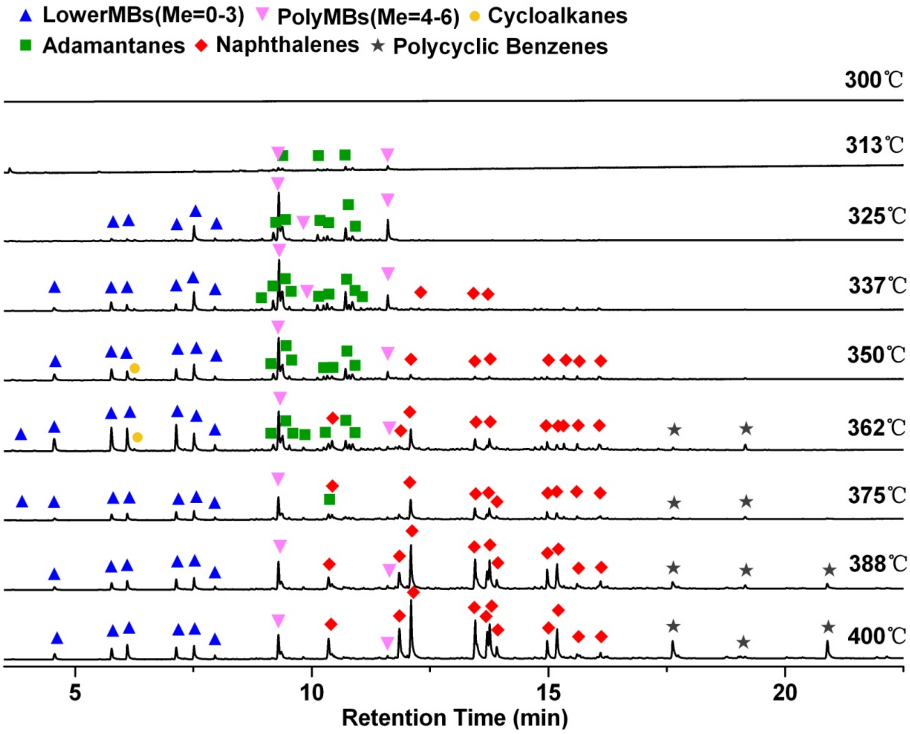
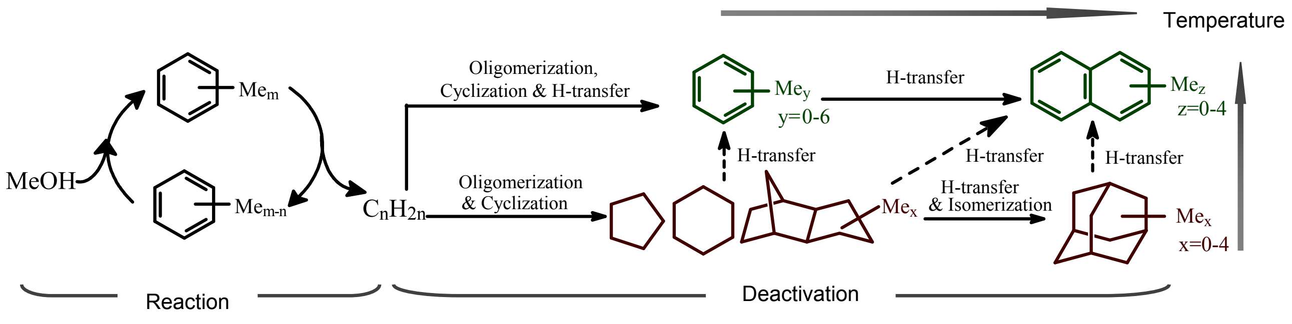


Figure 5-2 GC-MS analyses of retained materials in SAPO-34 catalysts after methanol conversion under the condition of temperature programmed increase from 250 to 400°C

Discussion of adamantanes and aromatics generation as comfined compounds in the cage of SAPO-34 in MTO reaction

The generation of aromatics and adamantane hydrocarbons and their possible evolution with temperature increase is proposed in Scheme S1. As suggested in hydrocarbon pool mechanism, [7] the reaction cycle runs successively in MTO: light olefins elimination from polyMBs followed by remethylation of the lower methylbenzenes (Scheme S1, left part). Propene and other light olefins, as the main products of MTO, are highly reactive in acid catalysis. On acid zeolites, these molecules may undergo oligomerization to form heavy products and further undergo cyclization and H-transfer to form the coke molecules.[3] Scheme S1 (right part) gives the possible route of adamantanes and aromatics generation as the trapped materials in SAPO-34 during methanol conversion. Oligomerization and cyclization of light alkenes in the CHA cage could generate cyclealkanes. Adamantane hydrocarbons possibly formed from the isomerization of some polycyclic alkane, such as endo-trimethylenenorbornane.[8] Diamondoid hydrocarbons with high H/C ratio (~1.6) possibly resulted from very modest H-transfer reaction and severe H-transfer or dehydrogenation caused the generation of H-unsaturated compounds, aromatics and polycyclic aromtics (H/C ratio <1). Our work also proved that adamantanes generation starting from propene conversion in SAPO-34 at low reaction temperature (Figure S6 and Table S2). In a previous study,[9] reaction of 1-hexene over SAPO-34 could also form confined adamantanes. The work presented in Figure 5-1 and 5-2 implied the adamantane conversion to aromatic coke species with reaction temperature increase.



Scheme1 Adamantanes and aromatics generation as comfined compounds in the cage of SAPO-34 in MTO reaction

Propene conversion over SAPO-34 at low temperature

Propene conversion was also performed over SAPO-34 catalyst at 300 and 350 °C on a microscale fluidized-bed reactor. Before test, the catalyst was loaded in the reactor and activated at 500 °C in He flow for 1 h and then the temperature was adjusted to the reaction temperature and propene was fed into the reactor. At time on stream of 1 h, the reaction was stopped and the catalyst was flushed and cooled very quickly. The discharged catalyst was dissolved in the HF solution and the coke species were extracted by CH_2Cl_2 solution and analyzed by GC-MS. As shown in Figure S6 and Table S2, the confined species in the catalyst after propene conversion at 350 °C was dominated with aromatic materials, while in the catalyst after reaction at 300 °C, beside aromatics, methyladamantane hydrocarbons were also formed in abundance. Table S2 gives the identification of the marked compounds.

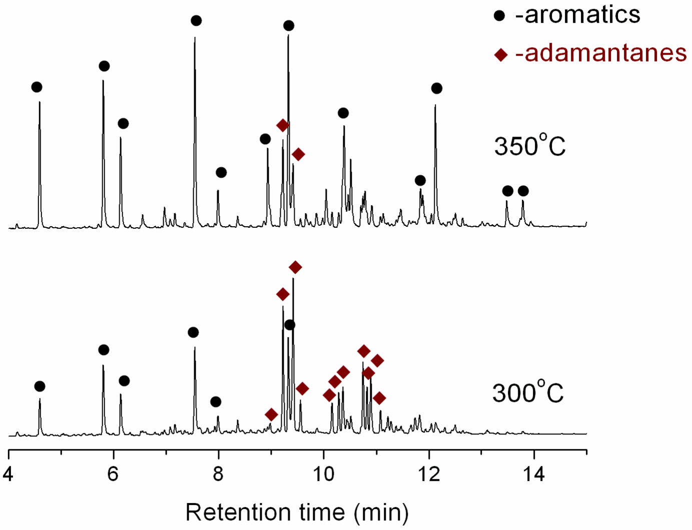


Figure S6 GC-MS analyses of retained materials in deactivated SAPO-34 catalysts after propene conversion at 300 and 350 °C.

Table S2 Identification of the retained compounds in deactivated SAPO-34 catalyst after propene conversion

Retention time (min)	Compounds	Retention time (min)	Compounds
4.59	Toluene	10.28	1,4-Dimethyladamantane, cis-
5.80	Xylene-1	10.3	1.4-Dimethyladamantane, trans-
6.13	Xylene-1	10.3	naphthalene
7.55	Trimethylbenezne-1	10.76	1,2-Dimethyladamantane
7.99	Trimethylbenzene-2	10.83	1,3,4-Trimethyladamantane, cis-
8.93	1-Ethenyl-3-ethyl-Benzene	10.90	1,3,4-Trimethyladamantane, trans
8.98	Adamantane	11.08	1-Ethyladamantane
9.22	1-Methyladamantane	11.89	1-Methylnaphthalene
9.33	TetraMB	12.12	2-Methylnaphthalene
9.41	1,3-Dimethyladamantane	13.48	2,7-Dimethylnaphthalene
9.56	1,3,5-Trimethyladamantane	13.79	2,6-Dimethylnaphthalene
10.16	2-Methyladamantane		

Confined materials formation in the nanocage of 8-ring SAPOs

SAPO-34 and other two 8-ring SAPOs, SAPO-18 and SAPO-35 with AEI and LEV nanocage (Figure S7) were employed in this study. They were synthesized by hydrothermal methanod followed the procedure reported in the literature.[2] The ratio of (Al+P)/Si is 16 for SAPO-18 and 12 for SAPO-35. The conversions were performed in a microscale reaction setup combined with a high-resolution microbalance (TEOM) for measuring the mass change of the packed catalyst bed in real time.[10] As shown in Figure S5, the induction period appeared in all the methanol conversion over SAPO-34, 18 and 35 at 300 °C, in which the fresh catalyst was transformed to the working catalyst. Since the beginning of the reaction with very low initial conversion, the catalyst mass presented a sharp increase until the deactivation occurred and the mass no longer increased.

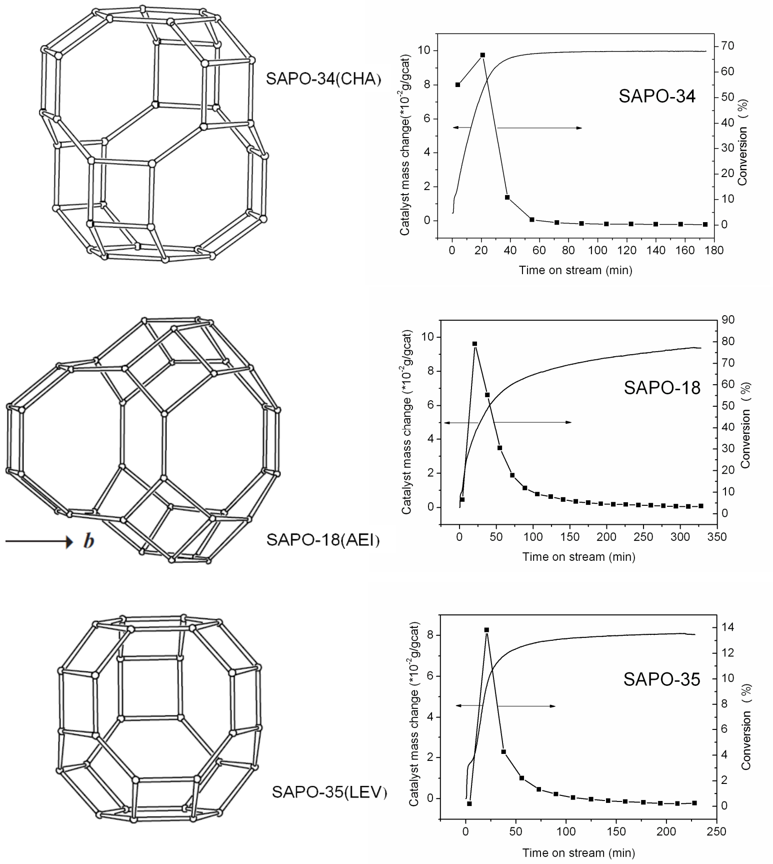


Figure S7-1 Methanol conversion and coke deposition with time on stream at 300 °C over SAPO-34, 18 and 35.

Under the reaction condition of low temperature, SAPO-34 catalyst with CHA cages provided the catalytic surrounding for adamantane hydrocarbons generation as confined materials. The trapped compounds analysis in this section indicated that as has been observed in SAPO-34, adamantane hydrocarbons also formed in the catalyst of SAPO-18 and SAPO-35. Dimethyladamantane and trimethyladamantane were predominant in SAPO-34 and SAPO-18. Adamantane and methyladamantane retained on SAPO-35, pocessing relatively small nanocage compared to SAPO-34 and SAPO-18.

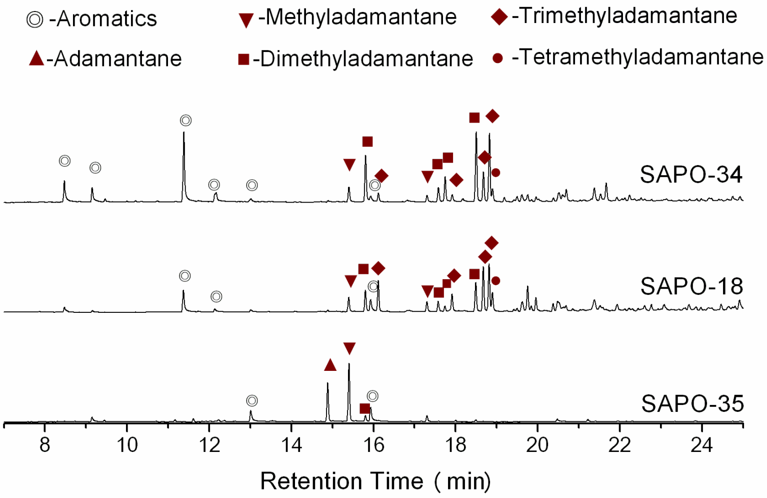


Figure S7-2 Determination of confined materials in SAPO-34, 18 and 35 with GC-MS after methanol conversion at 300 °C

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