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

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Formation of adamantane hydrocarbons and their confinement in SAPO-34 caused the long induction period and the quick catalyst deactivation in methanol conversion. *Via* ship-in-a-bottle synthesis, adamantane and methyladamantanes could be produced from methanol conversion in the cage of 8-ring SAPO catalysts under very mild reaction conditions.

The Methanol-to-Olefins (MTO) process has been regarded as the most successful non-petrochemical route for the production of light olefins from abundant resources of natural gas or coal.[1] In August, 2010, DMTO, the world's first commercial application of the MTO process with a production capacity of 600 000 tons of light olefins per annum, was proved to be completely successful in Baotou, China.[2] By employing a very effective catalyst comprising 8-ring SAPO-34 with CHA cages, extremely high olefins selectivity under mild conditions was attained.[3] As one of the key problems of the MTO reaction, coke generation over SAPO-34 has been intensively studied in the past two decades. In the MTO process, coke deposition is responsible for catalyst deactivation,[4] while some of the confined coke species also act as reaction centres for C–C bond formation from the C1 reactant, methanol.[5] For the sake of understanding the courses of methanol conversion and catalyst deactivation, it is essential to know the main characteristics of the coke, such as its composition, mode of formation, location, as well as how the coke affects the properties of the catalyst. Previous studies have proved that methanol conversion over SAPO-34 is based on a hydrocarbon pool mechanism, with polymethylbenzenes and their corresponding carbenium ions acting as the reaction centres,[6] and catalyst deactivation is generally accompanied by the progressive formation of polycyclic aromatic molecules and large coke fragments.[7] However, the observations presented in

this study showed an exception to this model. At temperatures of 300–325 °C, *i.e.*, about 100–150 °C below the optimal reaction temperature of MTO, besides aromatic coke species, diamondoid hydrocarbons, especially methyladamantanes, formed abundantly as retained compounds within the nano-cages (*ca.* 1 nm) of SAPO-34 and caused a quick deactivation of the catalyst. Adamantane is a saturated hydrocarbon consisting of three condensed cyclohexane rings arranged in an "armchair" configuration. Adamantane can be synthesized from carbenium ion rearrangement of a suitable precursor, such as multi-ringed norbornane or terpene hydrocarbons.[8] It is hard to imagine how this three-dimensional diamondoid structure can be formed in SAPO-34 during methanol conversion. The observation of the abundant generation of adamantane hydro-carbons is of great significance for the prevention of coke deposition in MTO, especially during the starting period in which methanol is fed to the reactor with a programmed increase in the temperature. It is also a meaningful finding for understanding the procedure and mechanism of the ship-in-a-bottle synthesis of polycyclic organics in the supercage of microporous catalysts.

For methanol conversion over the SAPO-34 catalyst at low reaction temperatures such as 300, 325 or 350 °C, an induction period existed, and quick deactivation of the catalyst also resulted (Fig. S1, ESI†). The initial conversion was very low. At a TOS of 2 min, the conversion was 52% at 350 °C, whilst almost no conversion occurred at 300 and 325 °C. With the extension of the reaction time, the conversion first increased to a high value and then sharply declined. It can be noted that the reaction period in which the conversion was keeping at a high level was prolonged if the reaction temperature was relatively high. Ethene, propene and butenes were the main products, among which, propene was the most important product.

After the reaction, the catalyst was flushed for a determined time and cooled down quickly. The completely deactivated catalysts at 300, 325 and 350 °C showed the colour of very light yellow, light yellow and yellow, respectively (Fig. 1a). It seems that not much coke formation occurred at 300 °C, while the amount of coke measured with thermal analysis was very close for the three deactivated catalysts, constituting about 8–9% of the sample weight. After dissolving the catalyst with a HF solution (20%), the confined organic compounds of the deactivated catalysts were extracted in a CH$_2$Cl$_2$ solution.

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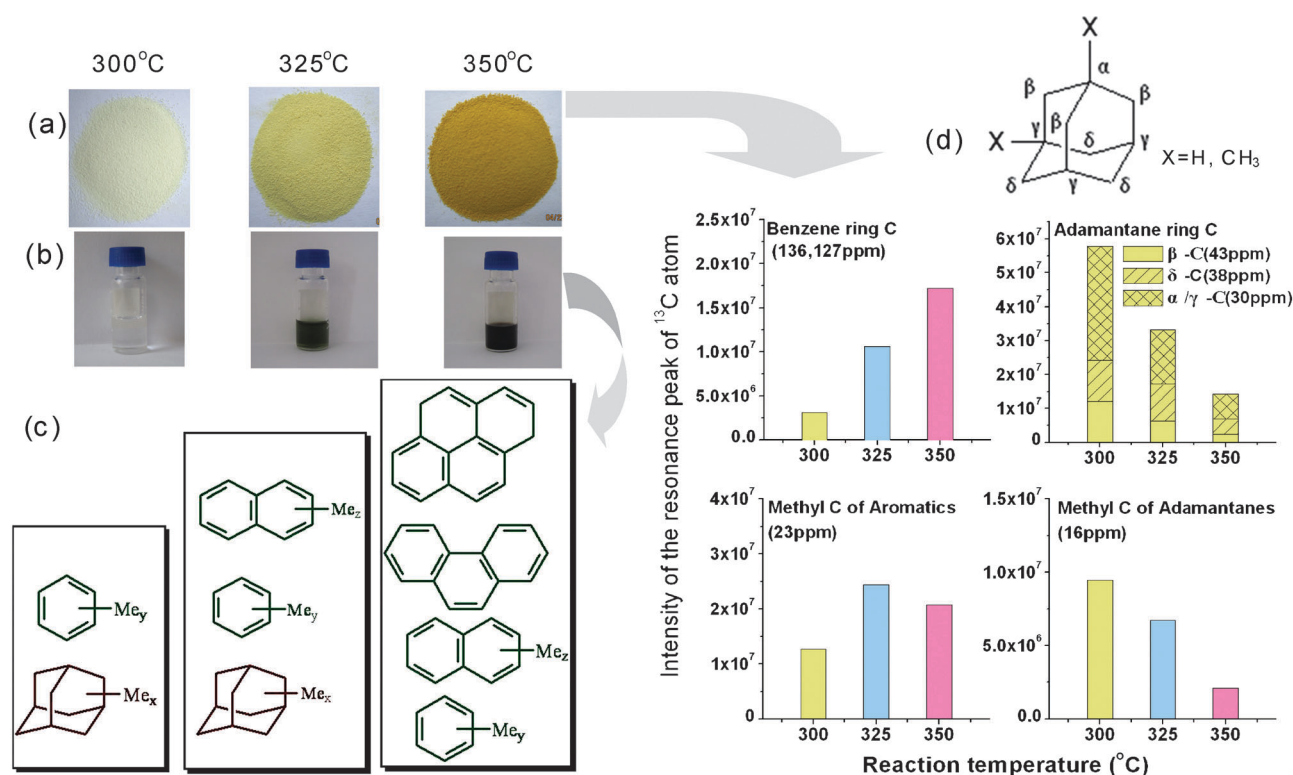
Fig. 1 Confined coke after methanol conversion at 300, 325 and 350 °C. (a) Deactivated catalysts; (b) extracted organics in CH$_2$Cl$_2$ solution from dissolved catalysts; (c) main coke species determined with GC-MS; (d) resonance peak intensity comparison of ^{1}H–^{13}C CP/MAS NMR spectra of confined organics.

Surprisingly, the solution from the completely deactivated catalyst at 300 °C was nearly colourless (Fig. 1b).

The extracted components of the coke species were analyzed by GC-MS and identified by the library of NIST08 and reference literature.[4,9] Based on the analysis (Fig. S2 and Table S1, ESI†), the main retained compounds of the deactivated catalyst are illustrated concisely in Fig. 1c. For the catalyst after reaction at 350 °C, methyl-substituted benzenes and methyl-substituted naphthalenes were predominant, while polycyclic aromatics, phenanthrene and pyrene also appeared among the extracted organics in low intensity. The formation of polycyclic aromatics caused pore blockage or acid site coverage, and was responsible for the deactivation of SAPO-34 catalysts.[4,7] A noteworthy and unexpected observation was that some species other than aromatics, namely, methyladamantane hydrocarbons, were detected among the retained materials of the catalysts after reaction at 300 and 325 °C. Especially in the catalyst deactivated at 300 °C, they were the predominantly formed species of the retained compounds. In an early work of Arstad and Kolboe,[5c] adamantanes were mentioned to be a minor part of the trapped species in the catalyst at the beginning of methanol conversion. In the study of Bleken et al.,[7e] after methanol conversion at 300 °C, retained compounds in catalysts with CHA topology, in SAPO-34 and in SSZ-13, were composed of aromatic hydrocarbons, and no adamantane derivatives were observed. In the present work, adamantane hydrocarbons appeared in abundance and were the most important materials among the coke species. The absence of naphthalenes and polycyclic aromatics in the deactivated catalyst after reaction at 300 °C implied that the deactivation at low temperatures was very

likely related to the generation and occlusion of this new kind of non-aromatic coke species, adamantane hydrocarbons, in the catalyst. The observation of adamantane hydrocarbons formation was consolidated by the measurement of ^{13}C MAS NMR and UV-Vis spectroscopy (Fig. S3, ESI†), and the intensity variation of adamantanes and aromatics with the reaction temperature is presented in Fig. 1d.

To study the confined coke formation in SAPO-34 at low reaction temperatures, a series of tests of methanol conversion were performed at 300 °C and stopped at a TOS of 17, 32, 47, 62 and 92 min. The trapped organics in the catalyst were analyzed by GC-MS, and their evolution with time on stream is highlighted in Fig. 2. At 17 min (Fig. 2a), the conversion was extremely low and the extracted organics could not be detected due to their very low concentration. The induction period was terminated with the appearance of PMB (pentamethylbenzene) and TetraMB (tetramethylbenzene) among the extracted organics after reaction for 32 min (Fig. 2b), and further intensity increase of these polymethylbenzenes (polyMBs) gave rise to an enhanced methanol conversion, with a maximum conversion value at 47 min (Fig. 2c). HMB (hexamethylbenzene) was also detected by GC-MS at a retention time of 13.85 min. Its low intensity stemmed from its high reactivity.[5b] Adamantanes began to appear at 32 min, intensified from 32 to 47 min and dominated among the retained organics after 47 min. During this period, methylbenzenes with less methyl group substitution (Me = 1–3), generated by the elimination of ethene or propene from polyMBs, tended to increase. PolyMBs and their protonated form, i.e., carbenium ions, are reaction centres in the MTO reaction for methanol adding and splitting of ethene and
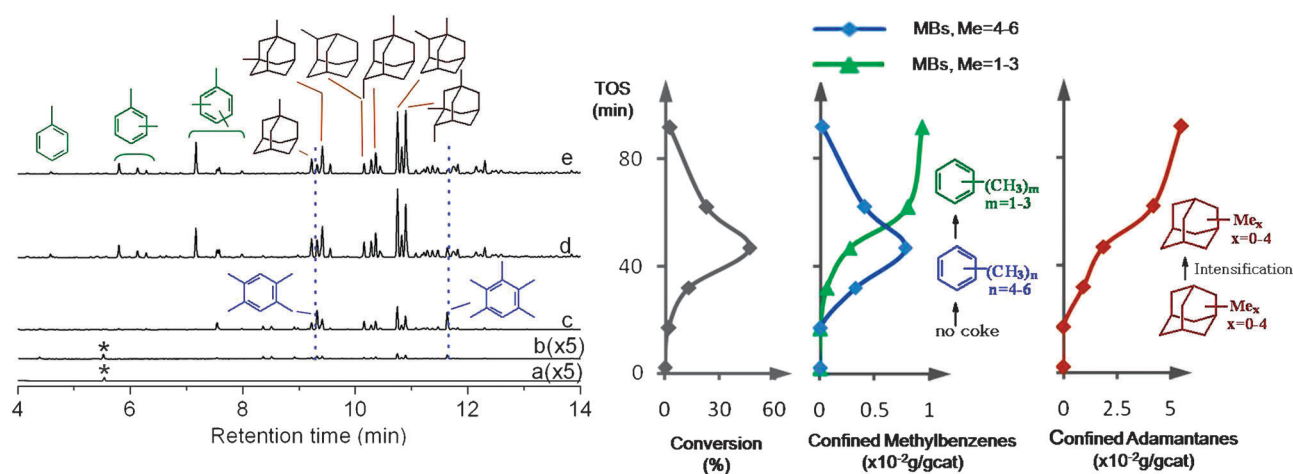
Fig. 2 GC-MS analyses (left) of confined organics after methanol conversion at 300 °C for 17 (a), 32 (b), 47 (c), 62 (d) and 92 (e) min; methanol conversion with time on stream (middle) and confined methylbenzenes and methyladamantanes variation with time on stream (right). *—internal standard.

propene products.[5,6] The sharp reduction of polyMBs corresponded to the occurrence of quick decrease in methanol conversion. A ^{13}C-methanol/^{12}C-methanol switch experiment proved the high reactivity of polyMBs as reaction centres of methanol conversion and also indicated that the diamondoid hydrocarbons were inactive in the reaction of MTO (Fig. S4, ESI†). Confined adamantanes in the catalyst could be transformed to aromatic organics at enhanced reaction temperature (Fig. S5 and S6, ESI†). A possible route to coke generation is given (Scheme S1, ESI†).

Besides SAPO-34, another two 8-ring SAPOs, SAPO-18 and SAPO-35 with AEI and LEV cage structures, were employed in the methanol conversion. As has been observed in SAPO-34, adamantane hydrocarbons also formed in the catalyst of SAPO-18 and SAPO-35 as confined materials. Dimethyladamantanes and trimethyladamantanes were predominantly formed in SAPO-34 and SAPO-18. Adamantane and methyladamantanes retained on SAPO-35 having smaller cages, as compared to SAPO-34 and SAPO-18 (Fig. S7, ESI†).

Our work illustrated that methanol conversion carried out at low reaction temperatures gave rise to long induction period and quick deactivation. Diamondoid hydrocarbons largely formed and retained in the SAPO-34 catalyst as a new kind of coke species. Different from polymethylbenzenes, the reaction centres of MTO, the confined methyladamantane molecules were inactive when in contact with the methanol feed. The accumulation of these cyclic and saturated hydrocarbons suppressed the successive generation of the hydrocarbon pool species and accounted for the quick deactivation of SAPO-34 at low reaction temperatures. 8-ring SAPO molecular sieves with cage structures such as CHA, AEI and LEV provided the catalytic environment for the formation of adamantane hydrocarbons as confined products in methanol conversion under the reaction condition of low temperatures. Together with the distinct and related work of CHA zeolite synthesis using adamantamine as the template,[10] a close connection could be predicted for the cage structure of the SAPO molecular sieves and the confined adamantane derivatives.

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