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Direct observation of hexamethylbenzenium radical cations generated during zeolite methanol-to-olefin catalysis: an ESR study†

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The generation of hexamethylbenzenium radical cations as the key reaction intermediate in chabazite-type molecular sieve acids (*i.e.*, H-SAPO-34 and H-SSZ-13) during the methanol-to-olefin process has been directly evidenced by ESR spectroscopy.

Apart from being of great technological relevance, unraveling the reaction mechanisms in many hydrocarbon conversions by zeolites and zeotype materials is of scientific interest because of its impact on developing new concepts of shape-selective catalysis. This is particularly the case of methanol-to-olefin (MTO) conversion, the alternative to produce ethene and propene from natural resources other than crude oil.[1] While much controversy remains on how an initial ethene C–C bond is formed from methanol or dimethyl ether, the hydrocarbon pool mechanism pioneered by Kolboe, Haw and their co-workers has now gained a clear consensus about the post-induction time MTO chemistry.[2,3] According to both experimental and theoretical findings reported thus far,[4] light olefins are produced *via* repeated methylation and dealkylation reactions of organic reaction centres which are aromatic in nature and are acting as catalytic scaffolds inside the void spaces of acidic microporous hosts. In addition, the type of major hydrocarbon pool species can differ according to the pore topology of zeolitic catalysts employed. For example, hexamethylbenzene (HMB)[2d] has been fairly well identified as the prime reaction intermediate in the small-pore silicoaluminophosphate (SAPO) molecular sieve H-SAPO-34 (framework type CHA) with cylindrical 20-hedral *cha* (6.7 Å in diameter and 10.0 Å in height) cages, the most widely studied catalyst for the MTO reaction.[1]

Undoubtedly, the observation and identification of reaction intermediates on a working catalyst is the key to making a success of mechanism elucidation. Given the role of zeolitic materials as a solid acid in MTO catalysis, on the other hand, the hydrocarbon pool species should first be generated as radical cations. It has long been recognised that the adsorption of neutral organic molecules, both aliphatic and aromatic, on acidic zeolites can yield their radical cations.[5] To our knowledge, however, no attempts to directly verify the existence of organic radical cations within microporous solid catalysts during MTO, especially when methanol is the only reactant introduced, have been successful yet. Here we present electron spin resonance (ESR) evidence that the hexamethylbenzenium radical cation ($HMB^{\bullet +}$), the protonated ring of which may be counterbalanced or stabilised by a zeolitic negative charge, is one of the true reaction intermediates in the hydrocarbon pool mechanism for the formation of light olefins over cage-based, small-pore molecular sieves like CHA-type catalysts. ESR spectroscopy has been useful for the characterisation of many paramagnetic species with one or more unpaired electrons.[6]

SAPO-34 with Si/Al = 0.21 and SSZ-13 with Si/Al = 5.1 were synthesised and converted to their proton form according to the procedures reported in the literature.[7] The characterisation results of these small-pore materials, including the powder X-ray diffraction patterns, SEM images, chemical compositions, BET surface area data and NH_3 temperature-programmed desorption profiles, can be found in the ESI.† A fixed-bed flow-type microreactor was used to carry out MTO over various zeolitic catalysts at atmospheric pressure. Methanol vapour diluted in N_2 flow was fed at a rate of 0.45 cm^3 h^{-1} (3.6 h^{-1} WHSV) into the reactor containing 0.1 g of the pelletized catalyst at 623 K. Further details of the MTO reaction are given in our previous work.[7a] Each catalyst after MTO was transferred to an ESR tube without exposure to ambient air, and ESR measurements were performed at 173 K on a JEOL JES-FA200 spectrometer at the X-band (9.17 GHz) with 100 kHz field modulation. The large organic materials deposited on the used catalysts were characterised *ex situ* by GC-MS total ion chromatography following the procedures reported elsewhere.[8]

Fig. 1 shows the ESR spectra developed after MTO as a function of time on stream (TOS) over H-SAPO-34 and its aluminosilicate version (*i.e.*, H-SSZ-13) at 623 K and 3.6 h^{-1} WHSV. Of particular interest is the ESR spectrum of H-SAPO-34 after 30 min on stream, when the catalyst is highly active, characterised by an 11-line hyperfine structure with a splitting of 6.4 G centred at g = 2.0031. Although less

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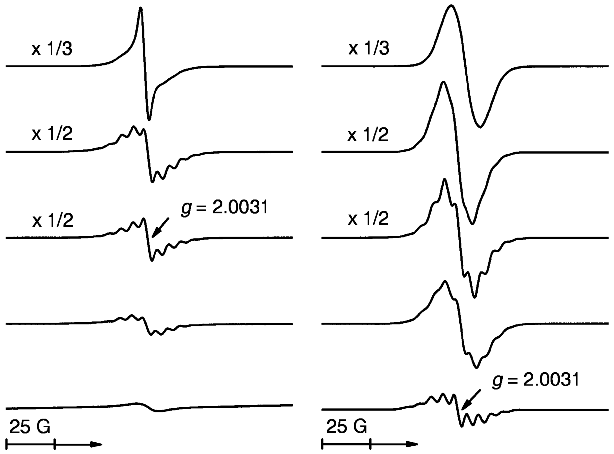

Fig. 1 X-Band ESR spectra at 173 K of paramagnetic organic centres generated in H-SAPO-34 (left) and H-SSZ-13 (right) during MTO for (from bottom to top) 15, 30, 60, 180 and 540 min on stream at 623 K and 3.6 h^{-1} WHSV.

pronounced, a similar result can also be obtained from the spectrum after the reaction over H-SSZ-13 for the same period of TOS. Because fresh H-SAPO-34 and H-SSZ-13 were found to be ESR silent, it is clear that paramagnetic organic centres are generated inside the *cha* cages of both catalysts during MTO. We should note here that the ESR spectra shown in Fig. 1 recorded after 30 min on stream or earlier are essentially identical to the spectrum of the radical cation obtained after the adsorption of neutral HMB on the large-pore zeolite H-mordenite (MOR, Si/Al = 5.0, Tosoh) (Fig. S3, ESI†), as previously reported.[5a] Furthermore, their hyperfine splitting and *g* values were found to be almost identical to those (6.5 G and 2.0027, respectively) reported for the 13-line ESR spectrum of UV-irradiated HMB molecules in concentrated sulfuric acid.[9] If such is the case, HMB$^{\bullet+}$, as well as its neutral counterpart (*i.e.*, HMB),[1] would then be the real reaction intermediate of MTO over these two CHA-type catalysts.

While the ESR signals from both H-SAPO-34 and H-SSZ-13 become stronger with TOS, their hyperfine splitting rapidly destroys. As a result, their spectra, when notably deactivated after 540 min on stream (Fig. S4, ESI†), are characterised by a distinct singlet signal with $g = 2.0031$. This indicates that the spin–spin interaction becomes stronger with TOS or upon the catalyst deactivation, typical for the formation of polycyclic aromatic hydrocarbon (PAH) species.[10] However, the rate of disappearance of hyperfine splitting, as well as that of increase in ESR signal intensity, is slower on H-SAPO-34 than on H-SSZ-13. This is not unexpected because the strength of strong acid sites is fairly lower in the SAPO material than in its zeolite analogue (Fig. S5, ESI†): the formation rate of PAH species in microporous solid acids responsible for the catalyst deactivation is known to be faster on the stronger acid sites.[11] It is worth noting that H-SAPO-34 changes colour from white to pale green after 540 min on stream and sustains this colour even after exposure to ambient air for 1 month. This suggests the exceedingly high stability of PAH radical cations in its *cha* cages to oxygen and water. HMB$^{\bullet+}$ also appears to be considerably stable, because our ESR experiments were carried out in an *ex situ* manner, but allowed us to clearly observe its formation in CHA-type catalysts at early TOS. In fact, the radical cations formed by adsorption of neutral HMB molecules on sulfated zirconia were reported to be stable for several days at room temperature.[12]

Assuming that the HMB$^{\bullet+}$ radical cations generated during MTO over H-SAPO-34 and H-SSZ-13 at 623 K for 30 min on stream are the sole paramagnetic species contributing to the observed signals and remain intact until the respective ESR experiments are over, the numbers of HMB$^{\bullet+}$ present inside their cha cages were calculated to be 0.3 and 1.3 ions per 10^4 cages in comparison with the intensity of the 2,2-diphenyl-1-picryl-hydrazyl (DPPH) radical, respectively. This strongly suggests that early in their lifetime only a very limited number of *cha* cages, probably those which are located on the surface/near-surface of catalyst crystallites, may contain HMB$^{\bullet+}$. The formation of a smaller number of HMB$^{\bullet+}$ ions in H-SAPO-34 than in H-SSZ-13 can be attributed again to the lower strength of strong acid sites in the former material.

For comparison, we also prepared the other structure type of cage-based, small-pore molecular sieves with SAPO and aluminosilicate framework compositions, *i.e.*, H-SAPO-17 and H-UZM-12 materials[8] with the ERI topology which contain 23-hedral *eri* cages with 6.3 Å in diameter and 13.0 Å in height, and recorded their ESR spectra after MTO at 623 K for different periods of TOS up to 540 min on stream. No detectable hyperfine splitting was found in all ESR spectra of used H-SAPO-17 catalysts. However, we were able to observe this phenomenon from H-UZM-12 after 60 min on stream, although the hyperfine splitting resolution was much poor compared with that of the spectra of CHA-type materials (Fig. S6, ESI†). Therefore, the generation of HMB$^{\bullet+}$ inside the cavities other than *cha* cages during MTO is, in principle, feasible. The failure of detecting the hyperfine structure from H-SAPO-17 may in our view be mainly due to the lack of strong acid sites in this ERI-type SAPO molecular sieve, unlike in SAPO-34 (Fig. S5, ESI†). It is also remarkable that the ESR spectra of the medium-pore zeolite H-ZSM-5 (MFI, Si/Al = 14, Tosoh) with two intersecting 10-ring channels after MTO for different periods (15–540 min) of TOS in the reaction conditions described above show no noticeable signs of hyperfine splitting except a singlet signal with $g = 2.0036$, irrespective of TOS.

Fig. 2 shows the GC-MS total ion chromatograms of CH_2Cl_2 extracts obtained by dissolving H-SAPO-34 in HF after MTO at 623 K and 3.6 h^{-1} WHSV for different periods of TOS. The structures annotated are selected peak identifications made by comparing the mass spectra with those in the NIST database.[13] The detectable aromatic hydrocarbon species formed on H-SAPO-34 after 60 min on stream or earlier, when the catalyst is still quite active, include polymethylbenzenes (PMBs) with 3–5 methyl groups, as well as HMB. Because a similar result was observed for the total ion chromatograms of the extracts from used H-SSZ-13 catalysts (Fig. S7, ESI†), we believe that the protonated counterparts of lower PMB homologues may also be the main reaction intermediates of MTO over these CHA-type catalysts. For example, pentamethylbenzene can be formed by the HMB side-chain alkylation and the subsequent olefin elimination.[3d] Because ESR did not allow us to detect lower PMB radical cations

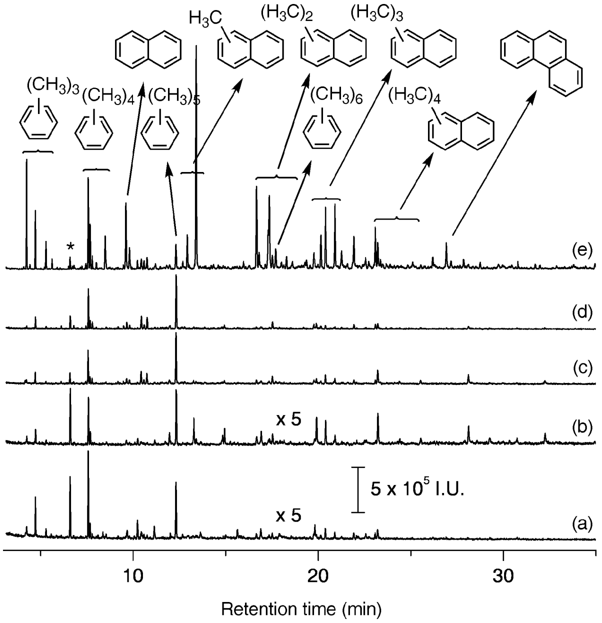

Fig. 2 GC-MS total ion chromatograms of CH_2Cl_2 extracts from H-SAPO-34 after MTO at 623 K and 3.6 h^{-1} WHSV for (a) 15, (b) 30, (c) 60, (d) 180 and (e) 540 min on stream, showing the identification of each of the observed peaks. The asterisk represents the mass signal of C_2Cl_6 used as an internal standard.

from all catalysts studied here, however, it appears that they may be much less stable than $HMB^{\bullet +}$, probably due to their lower molecular symmetry, which deserves further investigations. Fig. 2 also shows that the hydrocarbon species formed on H-SAPO-34 after 540 min on stream become very diverse. The dominant products include naphthalene, monomethylnaphthalenes and polymethylnaphthalenes with 2–4 methyl groups, as already reported,[8,14] together with phenanthrene. Given the highly symmetric nature of the intense ESR signal from this catalyst after MTO for the same period of TOS (Fig. 1), the PAH radical cations may be the species generated before their neutral ones, like the $HMB^{\bullet +}$ case.

In summary, our work provides clear experimental evidence that the $HMB^{\bullet +}$ radical cation, whose existence during MTO over zeolitic catalysts was until now pure speculation, is one of the true transition states of this heterogeneously very important reaction. Because the acidic microporous framework contributes to stabilise organic guest cations, spatial conditions could play a crucial role in persisting other aromatic radical cations like the heptamethylbenzenium ion suggested as important MTO reaction intermediates.[15] In that case, the optimisation of the framework topology of crystalline, microporous materials along with the control of their acidic properties will be one possible approach to directly identify major cationic hydrocarbon species other than $HMB^{\bullet +}$ during MTO over such solid catalysts using ESR spectroscopy.

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