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Electronic Supplementary Information

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

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Catalyst Preparation. CHA- and ERI-type molecular sieves with aluminosilicate and SAPO framework compositions were hydrothermally synthesised in Teflon-lined 45-mL autoclaves and converted to their proton form according to the procedures described in the literature.[1-4] Their preparation conditions are given in Table S1. As-made zeolitic materials were calcined in air at 823 K for 8 h to remove the organic structure-directing agents (SDAs) occluded. The calcined materials were then refluxed twice in 1.0 M NH_4NO_3 solutions (1.0 g solid per 50 cm^3 solution) for 6 h followed by calcination at 823 K for 4 h in order to ensure that they were completely in their proton form.

Characterisation. Product phase identification was carried out by powder X-ray diffraction (XRD) on a PANalytical X´Pert diffractometer (Cu K_α radiation) with an X´Celerator detector. All zeolites prepared here are highly crystalline and no reflections other than those from each material are observed. This can be further supported by the N_2 BET surface area data in Table S2, which were obtained on a Mirae SI nanoPorosity-XG analyzer. Elemental analysis was performed on a Jarrell-Ash Polyscan 61E inductively coupled plasma spectrometer in combination with a Perkin-Elmer 5000 atomic absorption spectrophotometer. Crystal morphology and average size were determined by a JEOL JSM-6510 scanning electron microscope (SEM). Ammonia temperature-programmed desorption (TPD) profiles were recorded on a fixed bed, flow-type apparatus linked to a Hewlett-Packard 5890 series II gas chromatograph with a thermal conductivity detector. A sample of about 0.1 g was activated in flowing He (50 cm^3 min^{-1}) at 823 K for 2 h, then 10 wt% ammonia was passed over the sample at 423 K for 0.5 h. The treated sample was subsequently purged with He at the same temperature for 1 h to remove physisorbed ammonia. Finally, the TPD was performed in flowing He (30 cm^3 min^{-1}) from 423 to 923 K at a temperature ramp of 10 K min^{-1}. Characterisation data for all zeolitic catalysts employed here are summarised in Table S2.

ESR measurements were performed at 173 K on a JEOL JES-FA200 spectrometer at X-band (9.17 GHz) with 100-kHz field modulation. The spin concentrations and g values of the paramagnetic organic centres formed were determined by comparing their intensities and resonant fields with those obtained from various amounts of the DPPH radical at $g = 2.0036$, respectively. The estimated error in spin concentration is ± 20%. The ESR spectrum developed after the adsorption of neutral hexamethylbenzene (HMB, 99%, Aldrich) molecules on a H-mordenite with Si/Al = 5.0 (Tosoh) was also recorded. The HMB adsorption procedure employed here is the same as that described in the literature.[5]

The coke materials formed on the zeolitic catalysts after MTO at 623 K for different periods of time-on-stream were extracted by a modification of the procedure originally developed by Guisnet group,[6] and their GC-MS total ion chromatograms were recorded on a Varian CP 3800 gas chromatograph equipped with a Varian 320-MSD mass selective detector, using electron impact ionization at 70 eV. The split ratio was 100:1, and the column used was a VF-5 capillary column (30 m × 0.25 mm) with flowing He (0.3 cm^3 min^{-1}). The temperature program ramps the column from 343 to 553 K at a rate of 4 K min^{-1}. The organic compounds extracted were identified in comparison with the NIST database.[7]

Catalysis. A fixed-bed flow-type microreactor was used to carry out MTO over various zeolitic catalysts at atmospheric pressure. Prior to the catalytic experiments, the proton form of each catalyst was routinely activated under flowing N_2 (120 cm^3 min^{-1}) at 823 K for 2 h and kept at 623 K to establish a standard operating procedure, allowing time for the reactant/carrier gas distribution to be stabilised. Then, 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. The reaction products were analysed online in a DS 6200 gas chromatograph equipped with a CP-PoraPLOT Q capillary column (0.25 mm × 25 m) and a flame ionization detector. The coulum temperature was maintained at 323 K for 5 min and increased to 513 K at a ramping rate of 10 K min^{-1}. CO_2 was separated using a packed Carbosphere column and analysed with a thermal conductivity detector. Conversion was defined as the percentage of methanol consumed during MTO. Dimethylether was not considered as a product. The yield of each product was calculated as the percentage of the amount (in mol) of methanol converted to hydrocarbons.

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Table S1. Synthesis conditions for small-pore molecular sieve catalysts employed in this study[a]

Catalyst	IZA code	Synthesis mixture composition[b]	*T*, K	*t*, day	Ref.
SAPO-34		$1.0DIPA\cdot1.0TEAOH\cdot1.0Al_2O_3\cdot1.0P_2O_5\cdot0.3SiO_2\cdot52H_2O$	448	2	1
SSZ-13	CHA	$2.0(TMAda)_2O\cdot15.0Na_2O\cdot1.0Al_2O_3\cdot32SiO_2\cdot1100H_2O$	423	5	2
SAPO-17		$1.0CH\cdot1.0Al_2O_3\cdot1.0P_2O_5\cdot0.1SiO_2\cdot61H_2O$	473	2	3
UZM-12	ERI	$13.0TEAOH\cdot2.0Me_4Et_2\text{-diquat-}5Br_2\cdot1.5KCl\cdot0.5Al_2O_3\cdot16.0SiO_2\cdot400H_2O$	373	14	4

[a] Crystallization was performed under rotation (60 rpm). [b] Fumed silica (Aerosil 200, Degussa) or colloidal silica (Ludox AS-40, DuPont) and pseudoboehmite (Catapal B, Vista) or $Al(NO_3)_3\cdot9H_2O$ (98%, Junsei) was used as Si and Al sources, respectively. Other starting reagents including organic structure-directing agents are the same as those described in refs 1-4.

Table S2. Characterisation data for MTO catalysts studied here

Catalyst	IZA code	Si/Al ratio[a]	Crystallite shape and average size,[b] µm	BET surface area,[c] $m^2\ g^{-1}$
H-SAPO-34	CHA	0.21	cuboids, 1	750
H-SSZ-13		5.1	heavily overlapped cuboids, 0.5 – 1	860
H-SAPO-17	ERI	0.04	needles, 0.5 × 3	610
H-UZM-12		6.5	rice grains, 0.6 × 1.1	680

[a] Determined by elemental analysis. [b] Determined by SEM. [c] Calculated from N_2 adsorption data.

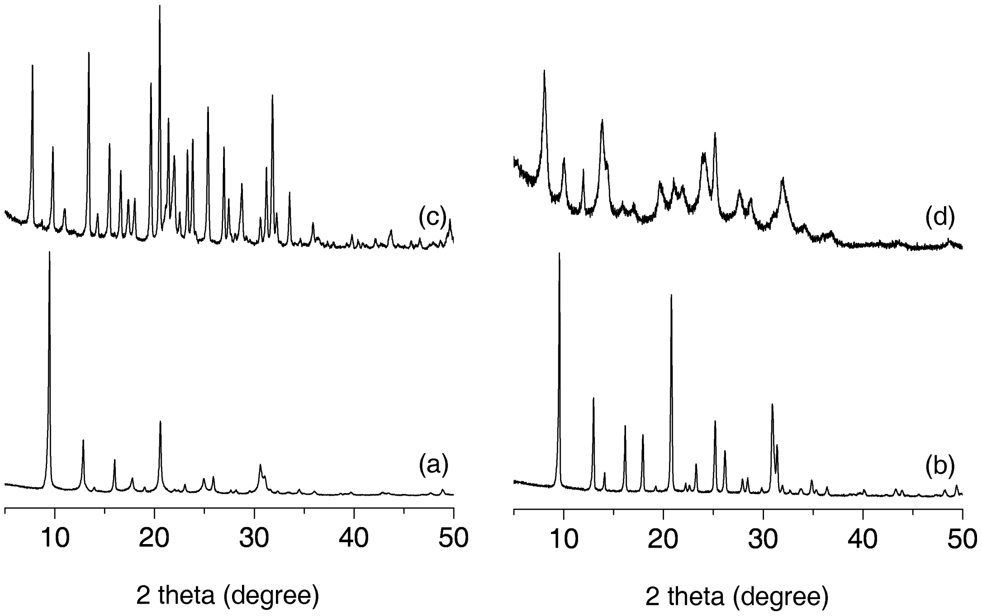

Fig. S1 Powder XRD patterns of the silicoaluminophosphate (left) and aluminosilicate (right) versions of CHA- and ERI-type molecular sieves in their proton form: (a) H-SAPO-34, (b) H-SSZ-13, (c) H-SAPO-17 and (d) H-UZM-12.

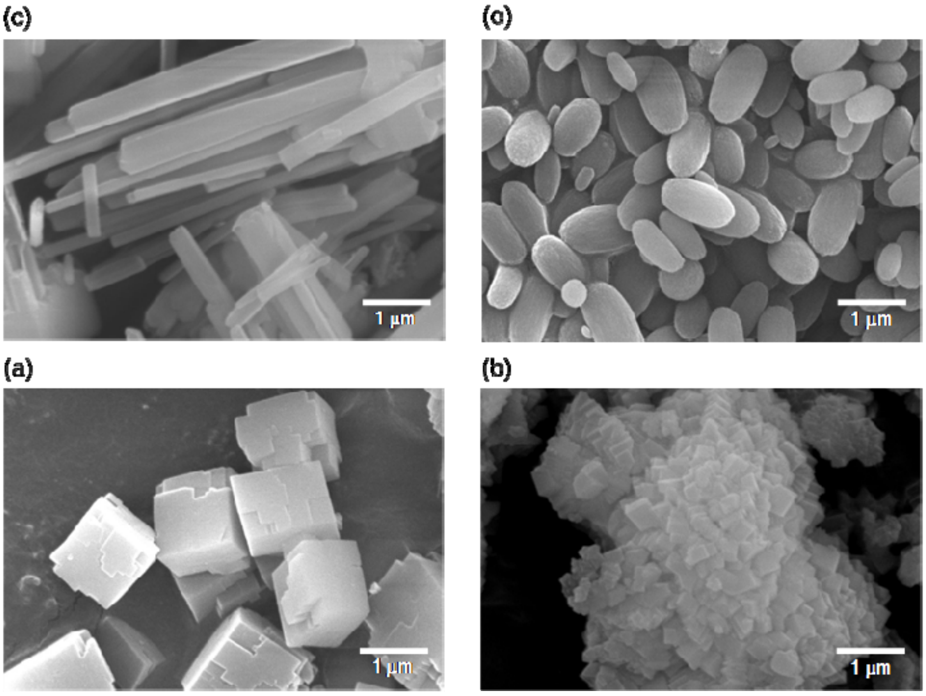

Fig. S2 SEM images of the as-made silicoaluminophosphate (left) and aluminosilicate (right) versions of CHA- and ERI-type molecular sieves: (a) SAPO-34, (b) SSZ-13, (c) SAPO-17 and (d) UZM-12.

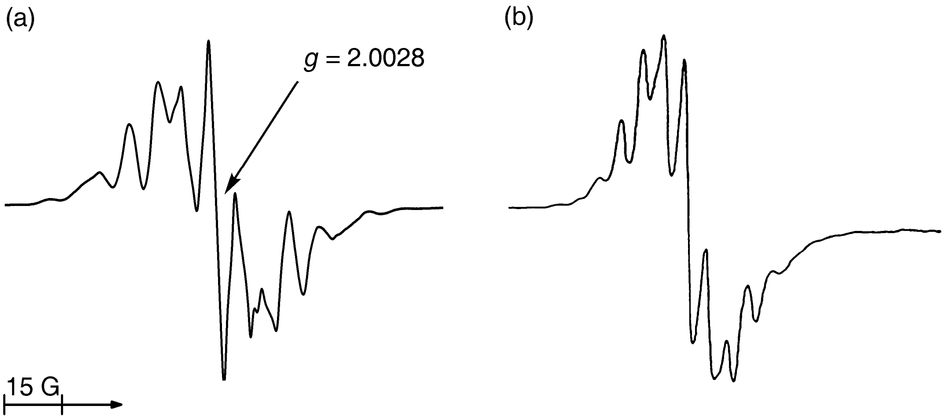

Fig. S3 (a) ESR spectrum at 173 K developed after adsorption of neutral HMB on H-mordenite with Si/Al = 5, which was obtained in our work. (b) ESR spectrum of HMB adsorbed on H-mordenite with Si/Al = 5.9 reported by by Corio and Shih.[5] Notice that both spectra are characterised by the essentially identical line shape.

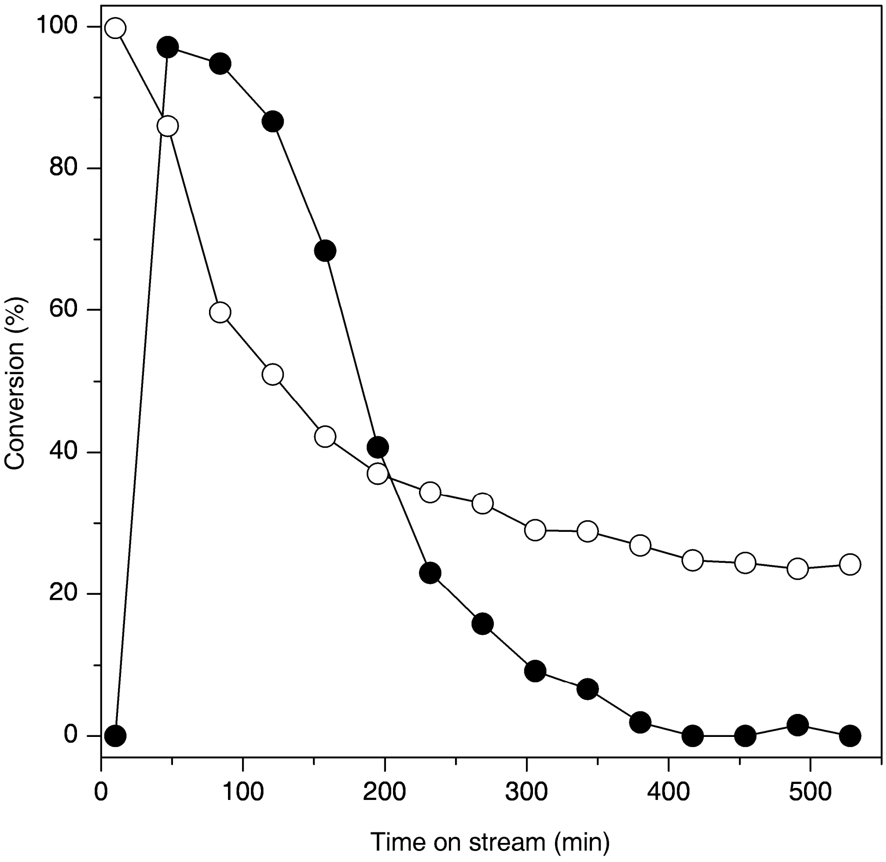

Fig. S4 Methanol conversion as a function of time on stream in MTO over H-SAPO-34 (●) and H-SSZ-13 (○) at 623 K and 3.6 h^{-1} WHSV.

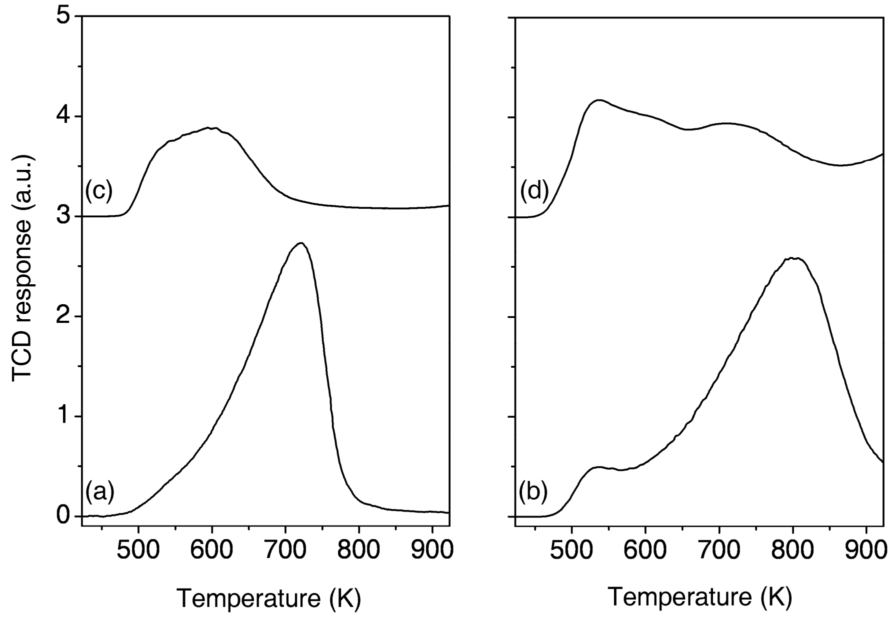

Fig. S5 NH_3 TPD profiles from (a) H-SAPO-34, (b) H-SSZ-13, (c) H-SAPO-17 and (d) H-UZM-12.

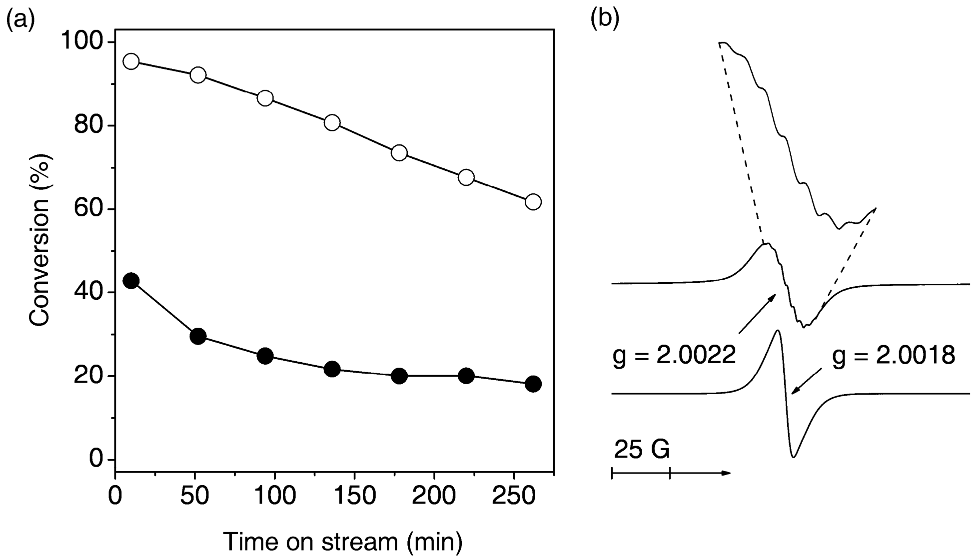

Fig. S6 (a) Methanol conversion as a function of time on stream in MTO over H-SAPO-17 (●) and H-UZM-12 (○) at 623 K and 3.6 h^{-1} WHSV. (b) ESR spectra at 173 K developed after MTO over H-SAPO-17 (bottom) and H-UZM-12 (top) at 623 K and 3.6 h^{-1} WHSV for 60 min on stream.

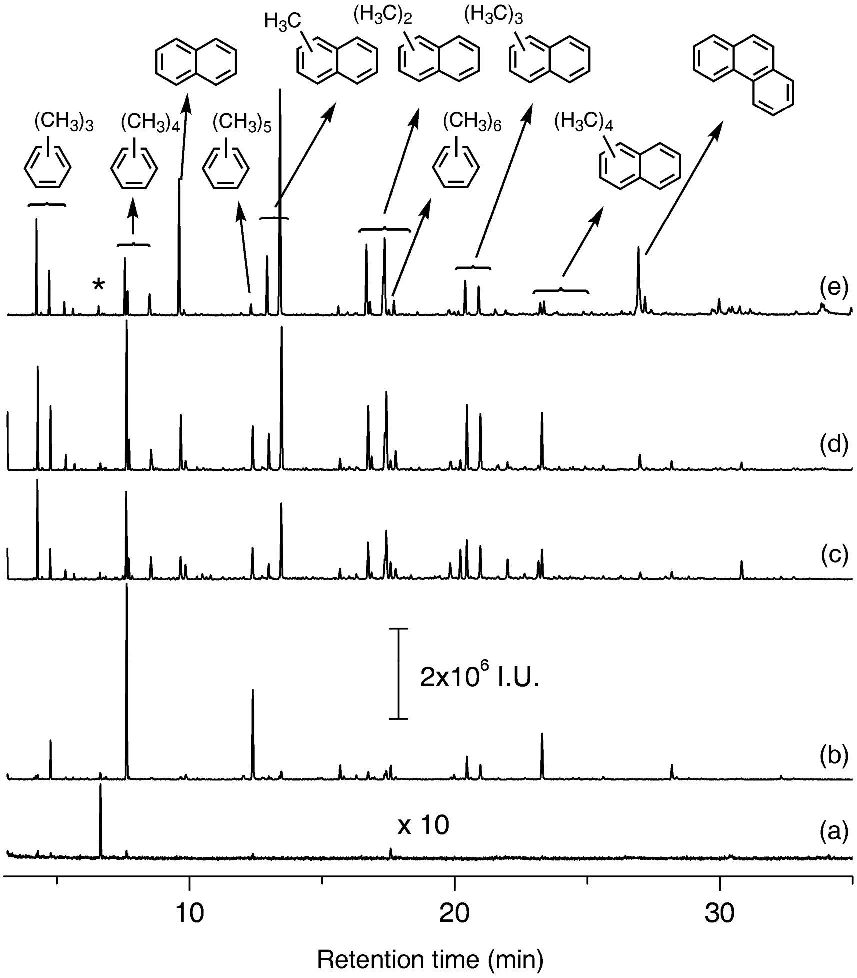

Fig. S7 GC-MS total ion chromatograms of the CH_2Cl_2 extracts from H-SSZ-13 obtained by dissolving in HF after MTO at 623 K and 3.6 h^{-1} WHSV for (a) 15, (b) 30, (c) 60, (d) 180 and (e) 540 min on stream, showing the identification of each of the observed peaks. The asterisk represents the mass signal of C_2Cl_6 used as an internal standard.