Operando infrared and inelastic neutron scattering studies of zeolite catalysed low-density polyethylene degradation

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SUPPLEMENTARY INFORMATION

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Experimental methods

Materials

The zeolite is a commercial sample from Zeolyst International. NH₄-ZSM-5 (CBV 8014, Si/Al 40) was calcined for 6 hours at 550 °C (ramp rate 1 °C/min) under static conditions to yield the proton form H-ZSM-5. LDPE was purchased from Sigma Aldrich (average $M_w \sim 4000$, 427772).

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) experiment

FTIR experiments were conducted using a Bruker Vertex 80, 32 scans (< 8 seconds) per measurement. Spectra were collected in DRIFTS configuration using the Praying Mantis accessory from Harrick Scientific. All spectra shown are recorded against dehydrated KBr as a reference material. The commercial zeolite was placed into the sample well of the Praying Mantis accessory (PM), and flushed with dry argon as the temperature was increased slowly to 400 °C, the temperature was held here for approximately 12 hours to ensure complete dehydration of the zeolite and PM chamber, and then cooled to 120 °C before the gas lines were sealed and the PM was transferred into a dry glove box to ensure that the zeolite remained dry. In the glove box, 11.1 mg of zeolite was combined with 3.7 mg of LDPE, and at room temperature were physically mixed by gentle grinding in a pestle and mortar for exactly 5 minutes to ensure even mixing. The mixture was transferred back into the PM and sealed, which was then taken back to the spectrometer to measure.

Spectra were recorded again under flushing with 30 ml/min of dry argon. The temperature of the mixture was increased by 5 °C/min to 80, 130, 170, 200 and 230 °C and then held for 5 minutes before measuring the spectrum that would correspond to that collected during INS. Further spectra were recorded from 230 °C to 400 °C to observe the recovery of the zeolite acid sites.

After recording, the data required normalisation for comparison due to differences in the scattering background. The spectrum of the LDPE/zeolite mixture shows lower scattering intensity, because the zeolite (which is highly scattering) is diluted. As the LDPE decomposes, in the raw data the background increases again. Spectra were normalised to the IR signals corresponding to the Si-O overtones of the zeolite at 1880 and 1938 cm⁻¹ that should be a constant intensity since they do not change during reaction.

Outlet gases were monitored by mass spectrometry, using a Pfeiffer Omnistar.

Inelastic Neutron Scattering (INS) measurements

The NH₄-ZSM-5 zeolite (approximately 11 g) was placed into a steel can connected to a gas delivery system and dehydrated under a flow of 20% oxygen in helium under flowing conditions to yield the dehydrated and proton form of the zeolite, H-ZSM-5. The reactor setup used here is described previously.¹ A furnace was raised, and the zeolite calcined for 6 hours at 550 °C. The steel can was flushed with helium to remove oxygen and cooled and sealed. The can was transferred into a dry glove box before it was opened. The dried zeolite was recovered (8.1 g), and combined with LDPE (2.7 g) to make up a 3:1 ratio by weight of zeolite to LDPE. The mixture was gently ground with a mortar and pestle for 5 minutes to ensure even mixing. Approximately 1.5 g of the zeolite/LDPE mixture was transferred back into the steel cans, sealed and reconnected to the gas delivery system. The mixture was flushed with helium and heated at 5 °C/min to the desired temperature for measurement; 80, 130, 170 or 200 °C and holding for 10 minutes. Outlet gases were monitored by mass spectrometry

(using a Hiden Mass Spectrometer) during this heating step. The reactor was allowed to cool, before being transferred back into the glove box and approximately 1.5 g of sample was recovered and sealed into aluminium cans sealed by indium wire. Measurements were carried out on TOSCA at ISIS Neutron and Muon Source, at 20 K, under experiment RB2220645.

Scanning Electron Microscopy (SEM) images

Samples were prepared by sprinkling powder onto a 10mm double sided conductive carbon tab. The samples were coated with 10 nm of chromium using a Quorum Technology Q150VS PLUS sputter coater. Images were take using a Jeol JSM-7900F field emission scanning electron microscope with 5kV accelerating voltage.

Thermogravimetric Analysis (TGA) measurements

TGA measurements were carried out on a TGA 5500 from TA Instruments. In both cases, the samples were ground gently. In the mixed sample, 75 mg of H-ZSM-5 was combined with 25 mg LDPE, and ground gently for 5 minutes to ensure even mixing, and a ~ 20 mg portion was placed in a platinum pan that was loaded into the TGA 5500. Under flowing nitrogen (25 ml min⁻¹) the temperature was increased by 5 °C min⁻¹ to 700 °C. LDPE was gently ground for 5 minutes to ensure a similar consistency in the pure sample as in the mixed sample, and the procedure repeated.

Powder x-ray diffraction (XRD) measurements

The PXRD pattern was collected on a Rikagu SmartLab with a 9 kW Cu source. Measurements were recorded over the range of 2 θ from 5 to 55°. The powder sample is placed on a goniometer and pressed to a flat surface for measurement. The measurement was recorded using 0.01° steps, 0.75° min⁻¹, and during measurement the sample spins at 1°min⁻¹ to avoid any preferred orientation of the powder.

Inductively Coupled Plasma (ICP) measurements

ICP was performed through MEDAC Ltd as a commercial service (https://medacltd.com/servicesview/metals-icp/). Measurements were conducted on a Varian Vista MPX CCD simultaneous axial ICP-OES instrument, based at MEDAC Ltd Laboratories.

FTIR-ATR of LDPE

An FTIR spectrum of the plastic was collected using ATR because DRIFTS of the pure LDPE resulted in artefacts. FTIR-ATR was collected on a Thermo Fisher iS10 with a diamond Smart ATR module.

Physicochemical characterisation

The diffraction pattern of the activated HZSM-5 zeolite confirms the crystallinity and structural integrity of the system (Figure S1). All Bragg peaks present are associated with the MFI framework,

and in good agreement with simulated peak positions based on literature cif files.² Inductively coupled plasma optical emission spectroscopy (ICP-OES) gave Al and Si contents as 0.91 and 42.89 wt. % respectively, translating to a Si/Al ratio of 45, in good agreement with the anticipated ratio of 40. Scanning electron microscopy shows the homogenous nature of the activated HZSM-5 particles, almost exclusively presenting smooth, aggregates, on the order of 1 μ m in size (Figure S2).



Figure S1: Powder X-ray diffraction patterns of the ZSM-5 used in this work (red; experimental), compared with the simulated data from the published cif file (black; simulated).²



Figure S2: Scanning electron microscopy images showing the activated commercial HZSM-5 catalyst used in this study. Primarily showing smooth, irregular aggregates of roughly 1 μ m in size.

TGA product formation



Figure S3: a) TGA data showing the influence of adding HZSM-5, and b) associated mass spectrometer data showing the evolution of small chain alkane and alkene products between 150 to 350 °C from the 75 % ZSM-5, 25 % LDPE mixture TGA findings in the main text. We note that other signals were traced, m/z of 2, 18, 44, 78, and 91, corresponding to hydrogen, water, carbon dioxide, benzene, and toluene/xylenes, however these showed no significant differences during the TGA data collection.

FTIR data and assignments

Wavenumber (cm ⁻¹)	Assignment	References
3736	External Si-OH	3, 4
3725	Internal Si-OH	5
3605	Bronsted acid sites	3
3500	Silanol nests	5

Table S1: Assignments of the zeolite in the O-H stretching regions

Table S2: Assignments of signals observed after mixing with LDPE

Wavenumber (cm ⁻¹)	Assignment	References
3694	Perturbed external Si-OH after	3, 4, 6, 7
	interaction with LDPE	
3450	Perturbed Bronsted acid sites	3, 4, 7
	after interaction with LDPE	
2955	Asymmetric CH₃ stretching	8
2925	Asymmetric CH ₂ stretching	8
2854	Symmetric CH ₂ stretching	8
1460	CH ₂ deformations	8







Figure S4: DRIFTS data showing the influence of adding LDPE to ZSM-5, compared to the ATR data of LDPE*, focusing on a) the wider C-H region ($4000 - 2500 \text{ cm}^{-1}$), and b) the C-C region ($2500 - 1200 \text{ cm}^{-1}$), and c) a difference spectrum of the 100% ZSM-5 and 75% ZSM-5, 25% LDPE systems in the region $4000 - 1300 \text{ cm}^{-1}$. d) Shows the influence of heating the mixed 75% ZSM-5, 25% LDPE from room temperature (RT) to 80 °C.

* The ATR-FTIR spectrum of the pure LDPE is shown instead of DRIFTS due to strong artefacts created in measuring undiluted LDPE. Subtle peak shifts are due to the different collection methods used.^{9, 10}



Figure S5: Mass-spectrometer traces from the DRIFTS experiments, showing the evolution of short chain alkanes and alkenes. Masses associated with CO₂, hydrogen, water, benzene, toluene, and xylenes were also collected but showed no significant change throughout the experiments.

Table S3: Further signals observed during reaction





Figure S6: DRIFTS data showing the influence of high temperatures (200 - 260 °C) on the reaction focusing on a) 3800 - 3000 cm⁻¹ and b) 3200 - 1300 cm⁻¹ regions.



Figure S7: INS spectra of A) LDPE/ZSM-5 mix compared to pure LDPE and pure ZSM-5, and B) data for the LDPE/ZSM-5 mixture, after being heated to different temperatures.

 Table S4:
 Literature assignments of the main features in the experimental LDPE INS spectra.

Wavenumber (cm ⁻¹)	Assignment based on Ref ¹³
132	Skeletal deformation

200	Maximum in v ₉
725	ρ(CH ₂)
1063	A _u τ(CH ₂)
1298	$B_{1g} \tau(CH_2)$
1371	$B_{1g} \tau(CH_2)$
1449	B_{2u} and $B_{3g} \omega(CH_2)$
2912	$v(C-H; CH_3 and CH_2)$



Figure S8: Mass spectrometer data from pretreatment of the INS 200 °C data, with a mixture of 75% ZSM-5, and 25% LDPE, showing the evolution of hydrocarbon signals from 100 °C. The temperature curve represents the set point of the reactor.



Figure S9: Schematic of LDPE cracking mechanism on HZSM-5.

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