Electronic Supplementary Information

Light alkane oxidation using catalysts prepared by chemical vapour impregnation: tuning alcohol selectivity through catalyst pre-treatment

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Experimental

The following procedure was used to prepare the 2.5wt% Fe/ZSM-5(30) material. H-ZSM-5(30) (Zeolyst, 0.975g) was placed into a Schlenk tube with a magnetic stirrer bar and heat treated under vacuum at 150°C for 2h. After cooling under vacuum, iron (III) acetylacetonate, $Fe(acac)_3$, (Sigma-Aldrich 99 minimum %, 177mg) was added and the tube re-sealed. The powders were manually agitated by shaking vigorously before the tube was re-evacuated at room temperature on a vacuum line (whose lowest attainable pressure was 10^{-3} mbar). The mixture was heated at 150 °C for 1h with magnetic stirring under continuous vacuum. The tube was then brought to atmospheric pressure in air and the sample removed for further heat treatments. Calcination in static air was performed at 550 °C for 3h. Reduction was performed at 550°C for 3h under flowing $5\%H_2/Ar$ or 100% He (20 ml min^{-1} , BOC gases). Note that the heat treatment under a reducing atmosphere was not preceded by calcination.

This same protocol was also used to prepare other Fe/ZSM-5(30) materials with differing iron loadings. In order to prepare the 1.25wt% Fe-1.25wt% Cu/ZSM-5(30) sample, $Cu(acac)_2$ (103mg, Sigma-Aldrich, 99% minimum) along with the required amount of $Fe(acac)_3$ was mixed in a glass vial by vigorous shaking prior to manual mixing with H-ZSM-5(30). This mixture was heated to 140°C for 1h under vacuum with magnetic stirring, followed by a calcination heat treatment at 550°C for 3h in static air. In all cases the resulting materials were highly uniform in appearance after the sublimation-deposition of the metal precursor and very little of the precursor remained in the Schlenk flask as evidenced by the lack of condensed metal precursor on the vessel walls. The initial amount of metal precursor is chosen to afford a specific theoretical metal loading since the organic moieties completely decompose during the calcination/reduction step (at 550°C). Actual metal loading was measured by ICP analysis (provided by Warwick Analytical Service (U.K.)).

For one preparation the H-ZSM-5(30) support was calcined in static air at 550°C for 3h and cooled to room temperature prior to being used in the iron deposition procedure. In this case ,the vacuum pre-treatment step was omitted.

$Fe(acac)_2$ (98% purity, Sigma-Alrdich) was also used to prepare an 0.4wt%Fe/ZSM-5(30) sample using the same methodology as described above, with the exception that the sublimation-deposition temperature employed was 160°C. The 'as-prepared' material was sifted to remove any dark brown aggregates which resulted from decomposition of the precursor during the deposition step. Such particulates were observed sitting atop the iron impregnated zeolite after the sublimation step. Calcination and reduction heat treatment on the catalysts were performed as outlined above.

2.5wt% Fe/SiO_2 was prepared using the methodology described from the zeolite based catalysts without the vacuum pre-treatment. Fe^{III} acetylacetonate was used as precursor and silica (Degussa Aerosil) as the support. This material was heat treated in static air at 400°C for 3h.

Autoclave reactor studies: The oxidation reactions were carried out using a stainless-steel autoclave (Parr reactor) containing a Teflon liner vessel having a total volume of 50 ml (*i.e.* working volume of 35ml). In a typical experiment, the catalyst (28 mg) was added to pure water (10ml) containing a measured amount of H_2O_2 (50 wt% H_2O_2). The system was pressurized with methane or ethane to the desired level (5.0 - 30.5 bar) after air in the reactor had been removed by purging three times with methane. The autoclave was then heated to the desired reaction temperature of 30-50 °C. Once the reaction temperature was attained, the solution was vigorously stirred at 1500 rpm and maintained at the reaction temperature for a fixed period. At the end of the reaction period the autoclave was cooled in ice to a temperature below 10 °C in order to minimise loss of volatile products and the reaction gas was removed for analysis in a gas sampling bag. The reaction mixture was filtered and analysed by ^{1}H-NMR using D_2O as a solvent and a calibrated TMS in $CDCl_3$ insert. Gas phase CO/CO_2 and C_2H_4 was determined by GC analysis on a Varian 450-GC equipped with FID & TCD detectors, methaniser and CP-SiL5CB column (50m, 0.33mm diameter, helium carrier gas). Gas phase O_2 was detected after reaction by TCD analysis, but not quantified.

These same procedures were also used for reactions in a larger Parr autoclave (100ml, working volume 70ml).

For catalyst reuse multiple reactions were performed and the catalyst recovered by filtration, followed by drying in air at 30°C overnight. The dried catalyst was then used in further testing without any treatments between runs. The catalytic data was the average of all runs done in that cycle. CHN analysis was performed on the dry materials by Exeter Analytical Services. DR-UV-Vis analysis was done as below.

STEM studies

Samples of Fe/ZSM-5(30) catalyst materials were prepared for STEM analysis by dry dispersing the catalyst powder onto a holey carbon TEM grid. High-angle annular dark field (HAADF) imaging experiments were carried out using either (i) an aberration corrected JEOL 2200FS STEM operating at 200kV, or (ii) an aberration corrected JEOL ARM-200F STEM operating at 200kV.

UV-Vis Spectroscopy

All spectra were recorded at room temperature in air after manual grinding of the samples using a ceramic mortar and pestle. Spectra were recorded on a Varian Cary 4000 spectrometer with range 900-200nm using a white PVC standard for a reference background. Data was recorded at room temperature and atmospheric pressure at a data interval of 1nm.

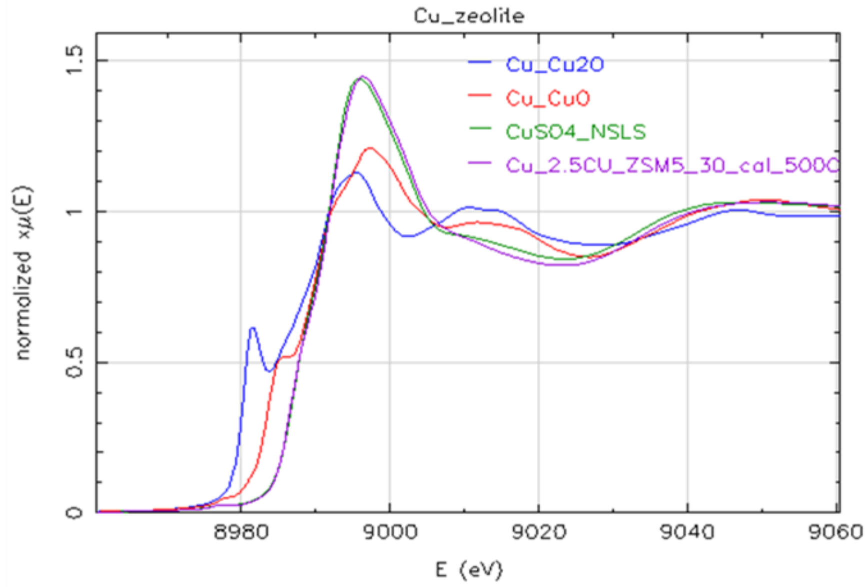
XAFS

Fe k-edge XAFS studies were carried out on the B18 beamline at the Diamond Light Source, Didcot, UK. Measurements were performed using a QEXAFS set-up with a fast-scanning Si (111) double crystal monochromator. The time resolution of the spectra reported herein was 10 min/spectrum (k_{max} = 15, step size 0.35 eV), and on average three scans were acquired to improve the signal to noise level of the data. All reference samples were diluted with cellulose and pressed into pellets to optimise the effective edge-step of the XAFS data and measured in transmission mode using ion chamber detectors. All transmission XAFS spectra were acquired concurrently with a Fe foil placed between I_t and I_{ref}. All Fe ZSM-5 samples were pressed as undiluted pellets and acquired in fluorescence mode using a 9 element solid state germanium detector[1] XAFS data processing was performed using IFEFFIT [2] with the Horae package[3] (Athena and Artemis).

References

1 A. J. Dent, G. Cibin, S. Ramos, A. D. Smith, S. M. Scott, L. Varandas, M. R. Pearson, N. A. Krumpa, C. P. Jones and P. E. Robbins in *B18: A core XAS spectroscopy beamline for Diamond*, *Vol. 190* Eds.: A. DiCicco and A. Filipponi **2009**.

2 M. Newville, *Journal of Synchrotron Radiation* **2001**, *8*, 322-324.
3 B. Ravel and M. Newville, *Journal of Synchrotron Radiation* **2005**, *12*, 537-541.



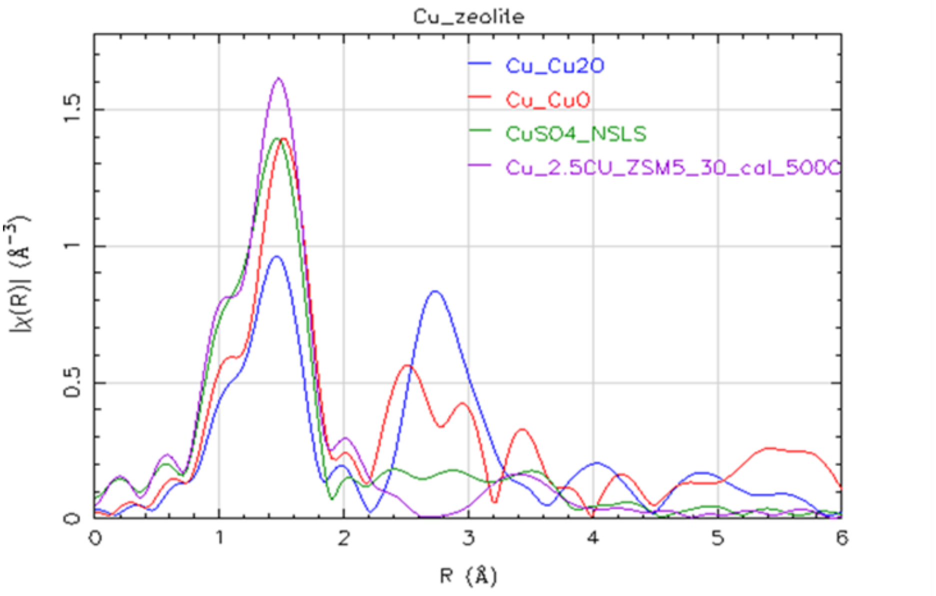


Figure S1. (a) XANES spectra for calcined Cu/ZSM-5(30) prepared by CVI and reference standards of Cu_2O, CuO and $CuSO_4$; (b) R-space data for the same. Cu is in the +2 oxidation state and highly distorted octahedral environment.

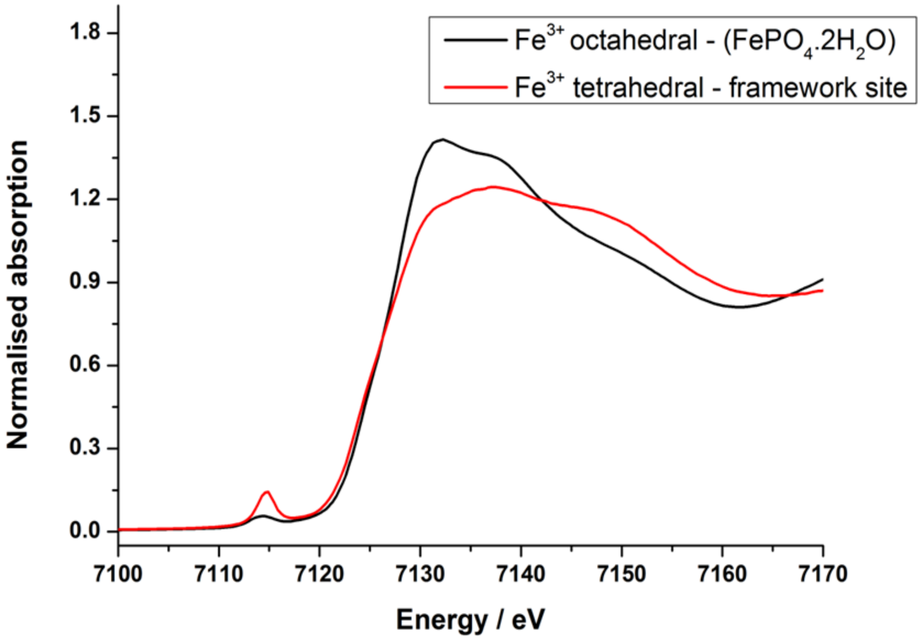


Figure S2. XANES spectra of tetrahedral and octahedral Fe species in reference standards used for this work.

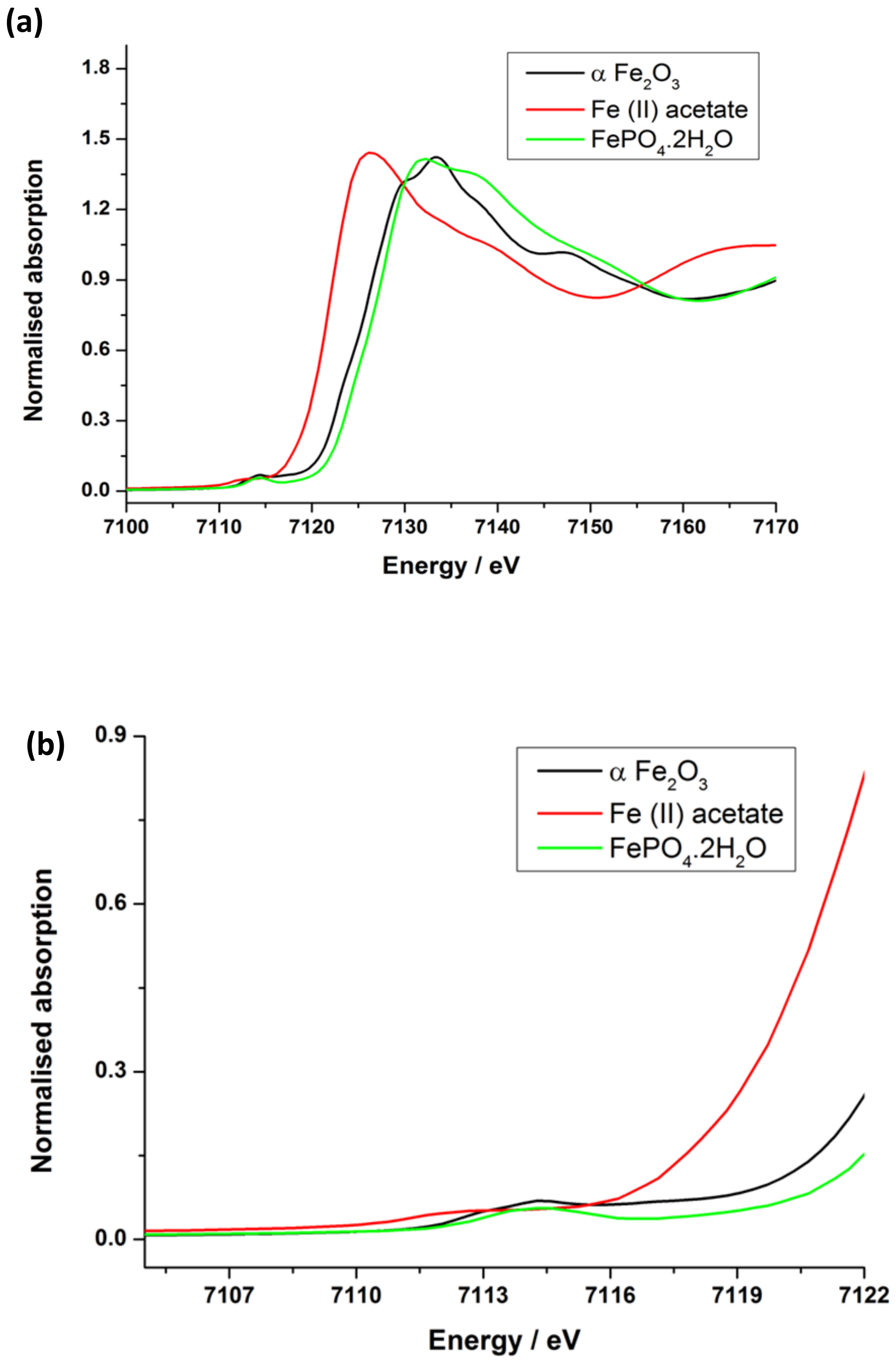


Figure S3. (a) XANES spectra of different octahedral Fe species and (b) expanded pre-edge feature of the XANES spectra for different octahedral Fe species**.**

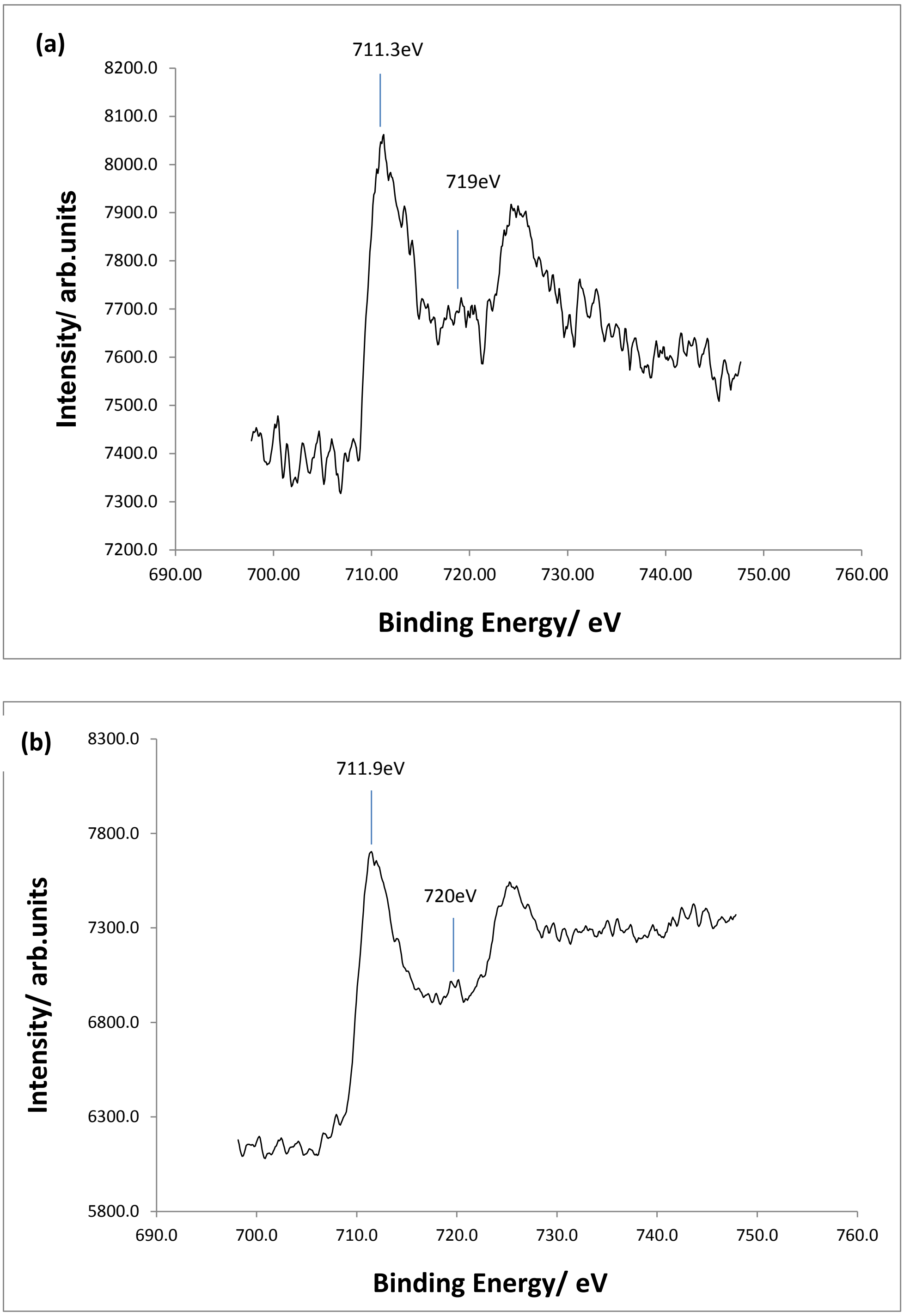


Figure S4. Fe $2p_{3/2}$ XPS spectra of (a) 0.4wt% Fe/ZSM-5(30) heated treated in air and (b) 0.4wt% Fe/ZSM-5(30) heated treated in hydrogen for 3h at 550°C. Spectra were measured at room temperature.

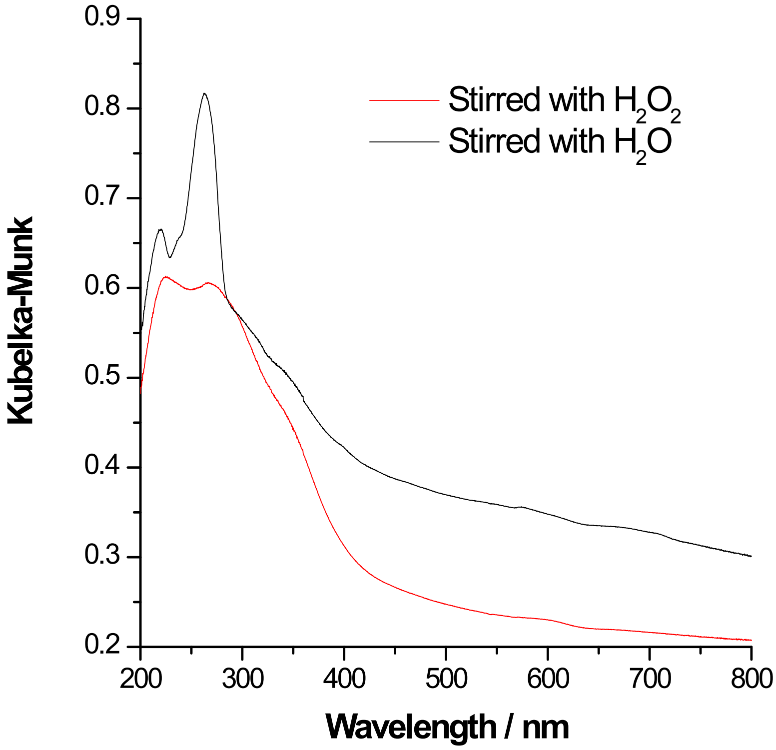


Figure S5. DR-UV-vis spectra of dried 1.1wt% Fe-ZSM-5(30) heat treated in hydrogen and stirred in water or H_2O_2(aq) under nitrogen atmosphere at 50° for 0.5h.

Table S1. Blank reaction of 1.1wt% Fe-ZSM-5(30) heat treated under hydrogen with hydrogen peroxide under an atmosphere of nitrogen.

CH_3OH C_2H_5OH μmoles	CH_2O CH_3CHO μmoles	HCOOH CH_3COOH μmoles	CH_3OOH C_2H_5OOH μmoles	CO_2 μmoles	H_2O_2used %
0.00	0.00	0.00	0.00	8.08	95.9

Test conditions: 54 mg catalyst; [H_2O_2]: 0.5 M; reaction volume 20ml; reaction temperature: 50 °C; stirring rate: 1500 rpm; reaction time: 0.5 h; P(N_2): 10bar.

Table S2. CHN analyses of fresh and used 1.1wt%Fe/ZSM-5(30) heat treated under hydrogen.

Condition	C wt%	H wt%	N wt%
Fresh	1.05	0.55	0.15
Used x1 CH_4	0.86	0.55	0.13
Used x1 C_2H_6	0.98	0.56	0.21

Test conditions as in Figure 8 of main paper. N.B. Single analyses performed.