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Electronic Supplementary Information (ESI) for the paper entitled:

A low temperature, isothermal gas-phase system for conversion of methane to methanol over Cu-ZSM-5

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S1 - Preparation of Cu-ZSM-5

NH_4-ZSM-5 (Si/Al = 12) was the parent zeolite for all catalyst preparations. NH_4-ZSM-5 (1 g) was added to a solution of $NaNO_3$ (1 g) in deionised water (150 ml), the mixture was stirred at room temperature for 24 hours. The catalyst was recovered by vacuum filtration, washed with deionised water and dried at 100 °C for 6 hours. The exchange procedure was repeated 3 times. Cu-ZSM-5 was then prepared by adding Na-ZSM-5 (1g) to a solution of Cu(II) acetate monohydrate in deionised water ($5x10^{-4}$ $moldm^{-3}$ Cu^{2+}, 0.25 dm^3). The mixture was stirred at room temperature for 24 hours, filtered under vacuum, washed with deionised water and dried at 100 °C for 6 hours. Freshly prepared Cu-ZSM-5 powders were pelletized in a 30 mm stainless steel die at 2 tons for 30 seconds, sieved to between 250-500 µm, then calcined in air using a muffle furnace at 500 °C for 4 hours before further testing.

S2 - Characterization of Cu-ZSM-5

Elemental analysis was performed by fusing Cu-ZSM-5 samples (20 mg) with sodium peroxide (0.5 g) in a zirconium crucible at 500 °C. The molten samples were quenched with water and 2M HCl added to form a resultant solution of 20 ml. The solution was analysed by ICP-OES using a PE Optima spectrometer. The Si/Al ratio of the parent zeolite was confirmed as 12. Cu content and Cu/Al ratio were determined to be 1.88 wt.% Cu and 0.28 Cu/Al respectively.

BET was used to determine surface area and pore volumes through N_2 adsorption using a Micrometrics Tristar II instrument. Samples were first heated at 100 °C for 1 hour followed by 350 °C for 2 hours under a stream of nitrogen to purge the zeolite surface of volatiles.

TEM was performed using an FEI Tecnai F20 electron microscope. Cu-ZSM-5 samples were suspended in 95% ethanol solution and adhered to a copper microgrid before imaging from 9.9-880 kx magnification. TEM showed an ordered structure indicative of the zeolite channel framework, copper particles were visible at high magnification with a maximum diameter of approximately 10 nm, see Figure S2.1.

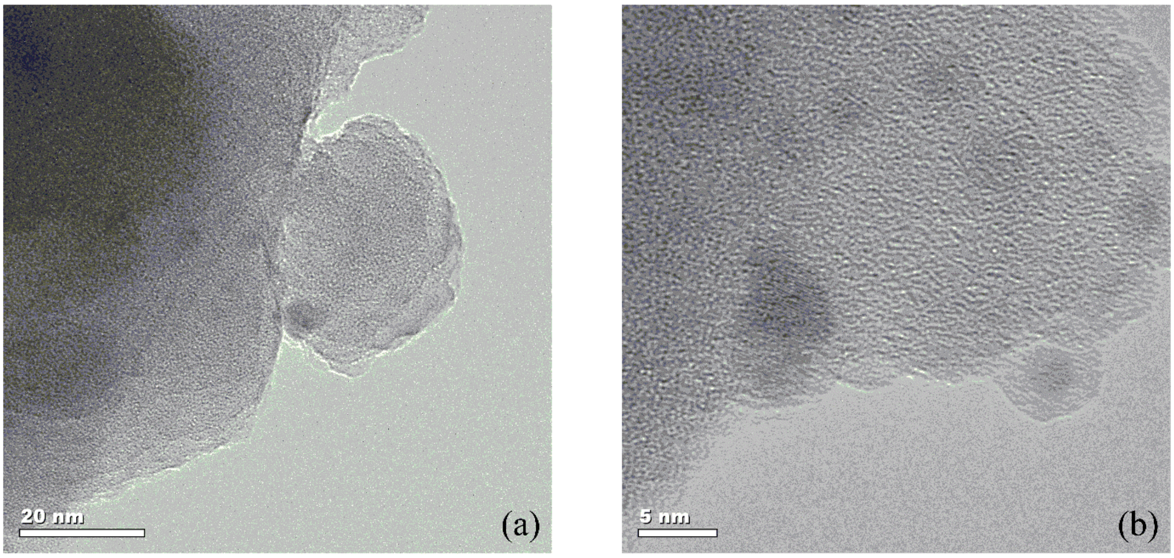


Fig. S2.1 - TEM images of Cu-ZSM-5 after ion exchange with copper and calcination. Zeolite framework and dispersed copper were visible at (a) 195k magnification; with high focus on copper-containing regions at (b) 490k magnification.

S3 - *In-situ* UV-vis Analysis of Catalyst Activation

Figure S3.1 shows the *in-situ* UV-vis rig used. Pre-calcined, pelletized Cu-ZSM-5 samples (0.7 g) were loaded into a quartz reactor, secured with quartz wool, and aligned in a tube furnace. Temperature was regulated by a thermocouple placed within the catalyst bed. Gas feeds were regulated by mass flow controllers. Gases were dried by flowing through a silica trap, followed by a cold trap to condense water from the feed. Prior to activation, samples were pre-reduced at 500 °C for 3 hours under a flow of Ar (50 sccm). Samples were treated by the following methods in order to activate the catalyst: (a) heating for 1.5 hours at 50 °C intervals from 100 to 350 °C under a flow of NO (25 sccm, 1% in Ar); (b) heating for 1.5 hours at 50 °C intervals from 100 to 400 °C under a flow of N_2O (25 sccm, 5% in Ar); (c) heating for 6 hours at 400 or 450 °C (indicated in text) under a flow of O_2. Following activation at each temperature interval, the catalyst bed was cooled and UV-vis measurements were taken at ambient temperature.

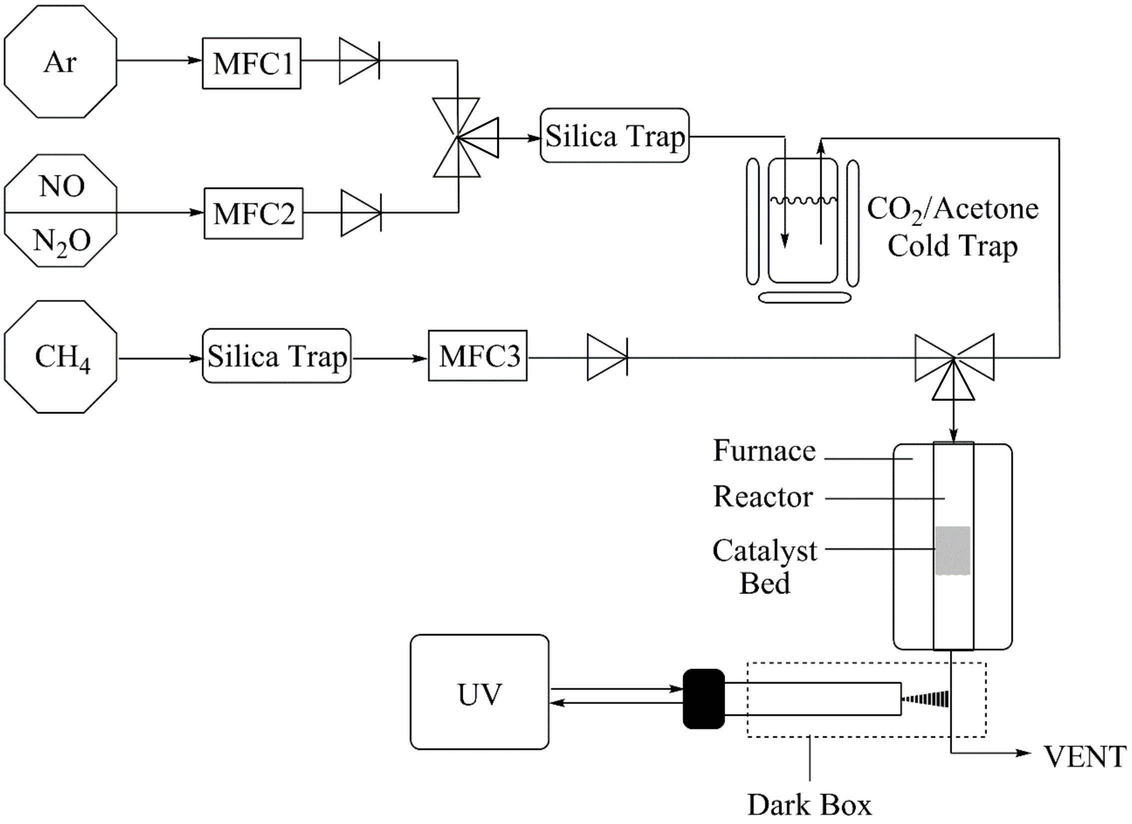


Fig. S3.1 - Fibre-optic probe, UV-vis spectrometer and quartz plug-flow reactor rig.

All measurements were made by diffuse reflectance using a Hellma 668.006-UVS probe positioned 1 mm from the catalyst bed and connected to a PerkinElmer Lambda 650 S UV-vis spectrometer by fibre optic cables. The reactor was mounted with flexible tubing, allowing repositioning of the catalyst bed *in-situ* under the probe for spectral acquisition. During measurement, the probe, reactor and catalyst bed were enclosed in a dark box to minimise interference from ambient light. The parent zeolite NH_4-ZSM-5 was used to provide baseline measurements. Spectra were recorded in transmission (% T) mode and converted to Kubelka-Munk. All spectra presented were the result of the superposition of 8 individual scans.

The UV-vis band observed around 450 nm was attributed to the bent mono(μ-oxo) dicopper core, visible during heating in NO above 100 °C (Figure S3.2), or in N_2O above 200 °C (Figure S3.3). UV-vis analysis of the same catalyst during activation in O_2 for 6 hours is also included in Figures S3.2 and S3.3 for comparison. The latter represents a typical high temperature oxygen activation procedure known to result in observation of the active core.

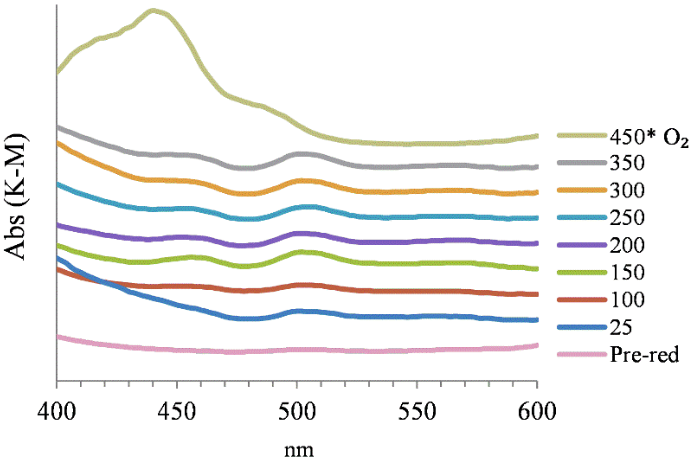


Fig. S3.2 - Normalised diffuse reflectance UV-vis spectra during pre-reduction at 500 °C in Ar for 3 hours, followed by activation in NO (25 sccm, 1% in Ar) for 1.5 hours at the temperature indicated. "450* O_2" indicates a separate activation at 450 °C in O_2 for comparison. Core absorption band visible at 455 nm in NO and 440 nm in O_2.

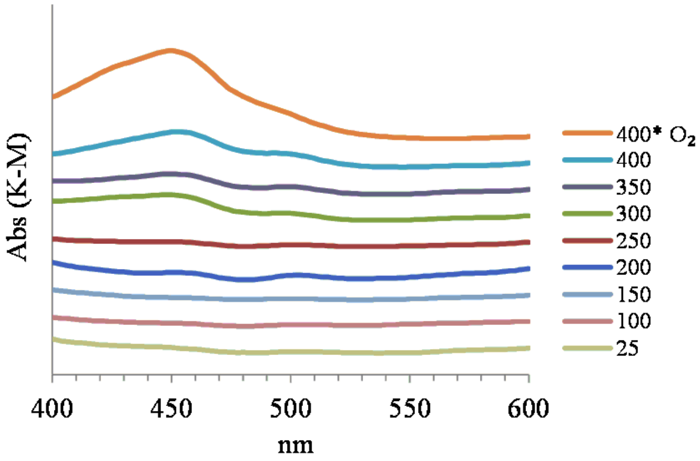


Fig. S3.3 - Normalised diffuse reflectance UV-vis spectra during activation in N_2O (25 sccm, 5% in Ar) for 1.5 hours at the temperature indicated. “400* O_2” indicates a separate activation at 400 °C in O_2 for comparison. Core absorption band visible at 455 nm in N_2O and 450 nm in O_2.

A second UV-vis band was also observed at 500 nm during activation in O_2, NO and N_2O. This was considered to be a zeolite feature arising from the use of NH_4-ZSM-5 as an instrument baseline, as it was observed regardless of the oxidant used. Observation of the same band during blank activation with Na-ZSM-5 suggests the band is not relevant to the partial methane oxidation process.

S4 - Reaction with Methane, Aqueous Product Extraction and GC Analysis

The following procedure was also performed in the UV-vis rig detailed in Figure S3.1. Following activation separately in NO at 150 °C, N_2O at 200 and 300 °C or O_2 at 500 °C, Cu-ZSM-5 samples were exposed to methane (50 sccm, 1% CH_4 in Ar) at 150 °C for 1 hour. The reactor was then cooled to ambient temperature and flushed with Ar. Samples were removed from the reactor and the products extracted by stirring vigorously in deionised water (1.5 ml) for 24 hours. The resulting suspension was centrifuged for 5 mins at 2000 rpm and the supernatant solution passed through a syringe filter (13 mm, 0.45 µm nylon membrane). Analysis was performed using a PerkinElmer Clarus 500 GC, equipped with an FID and a Supelco 25353 Carbowax® Amine column (30 m x 530 µm, 1 µm film). 2 µl samples were injected at 150 °C and the column was heated from 60 to 120 °C (10 °C/min). Methanol was confirmed as the sole product by reference sample, with quantification by calibration curve.

The following blank experiments were performed to confirm the observation of methanol as due to interaction of NO or N_2O with Cu-ZSM-5 catalysts. In both cases, the method was followed as described above, but with the following modifications:

- Na-ZSM-5 was used as a catalyst, replacing Cu-ZSM-5. No methanol was detected following GC analysis.
- Activation was performed in O_2 (50 sccm, 100%) for 6 hours at 150 °C and 200 °C separately. No methanol was detected following GC analysis.

S5 - Catalytic Experiments with NO and N_2O

Figure S5.1 shows the *in-situ* MS rig used for catalytic testing. Pre-calcined, pelletized Cu-ZSM-5 samples (0.7 g) were loaded into a quartz reactor, secured with quartz wool, and aligned in a tube furnace. Temperature was regulated by a thermocouple placed within the catalyst bed. Gas feeds were regulated by mass flow controllers. A gas-mixing setup was employed to facilitate catalyst activation, reaction with methane and product extraction using steam, the latter was introduced via a saturator with argon as carrier gas. All tubing was heated to prevent condensation of steam before contact with the catalyst bed. A 4-way valve was used to allow pre-mixing of gas feeds before introduction to the catalyst, maintaining signal stability during mass spectrum acquisition. The reactor outlet was designed to permit *in-situ* analysis of products by MS, or to facilitate condensation of products by passing the gas stream through a cold trap of CO_2/acetone at -78 °C. The latter offers a functional method of product separation in a batch type process.

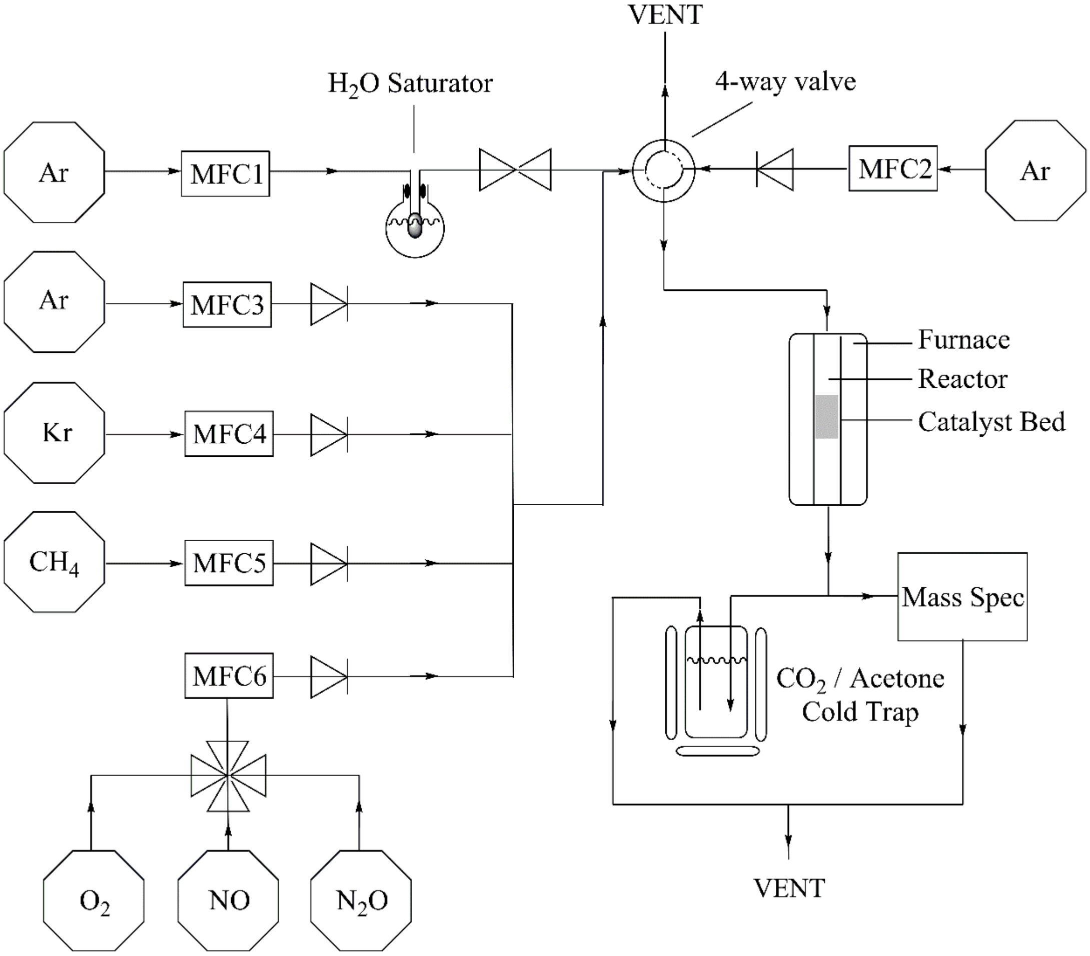


Fig. S5.1 - *In-situ* MS rig for catalytic testing.

For catalytic testing using NO as oxidant, Cu-ZSM-5 was introduced to the reactor under an initial flow of Ar (50 sccm) at ambient temperature. A pre-mixed feed of NO/Kr/Ar (25/10/15 sccm) was prepared and vented for 15 mins, before being introduced to the reactor and MS. The oxidant mix was monitored at ambient temperature for 15 mins to confirm a stable baseline. The catalyst was then heated from 20 to 150 °C (10 °C/min) and maintained at 150 °C for 2 hours.

For catalytic testing using N_2O as oxidant, Cu-ZSM-5 was introduced to the reactor under an initial flow of Ar (50 sccm) at ambient temperature. A pre-mixed feed of N_2O/Kr/Ar (25/10/15 sccm) was prepared and vented for 15 mins, before being introduced to the reactor and MS. The oxidant mix was monitored at ambient temperature for 15 mins to confirm a stable baseline. In the first instance, the catalyst was then heated from 20 to 300 °C (10 °C/min) and maintained at 300 °C for 2 hours. In a second experiment, heating was performed from 20 to 200 °C (10 °C/min) and maintained at 200 °C for 2 hours.

Immediately following oxidation in NO or N_2O, the temperature was set to 150 °C and the reactor purged with dry Ar (50 sccm) for 10 mins. A pre-mixed feed of CH_4,/Kr/Ar (25/10/15 sccm) was vented for 10 mins before being introduced to the reactor and MS. The reactant mix was maintained at 150 °C for 1 hour, followed by purging of the reactor with dry Ar (50 sccm). Finally, at a constant temperature of 150 °C, a feed of dry Ar/Kr (40/10 sccm) was introduced for 10 mins to confirm a stable baseline. Part of the dry Ar feed was then diverted through a bubbler containing water at 20 °C, such that a composition of Ar/Kr/H_2O (39/10/1 sccm) was passed over the catalyst. The products desorbed were monitored by MS, complete desorption was typically noted between 2-3 hours.

Mass spectra were recorded using a Hiden Analytical instrument. The total gas flow rate was maintained at 50 sccm constantly throughout catalytic testing. Kr was used as an internal standard at 1 % of total flow. The following traces (m/z in parenthesis) were monitored: CH_4 (15), O_2 (16), H_2O (18), CO/N_2 (28), NO (30), CH_3O^+ (31), Ar (36), CO_2/N_2O (44), DME (45), Kr (82). Relative SEM = 1, except for CH_3O^+ (31) relative SEM = 0.1.

Raw mass spectra were baseline corrected and normalised using the Kr trace as internal standard. Normalised traces were smoothed to an average of ten data points and the relevant product desorption curves integrated to quantify the raw product. The data was converted to molar values using the response factor for each product as determined by calibration curves. Final data was therefore presented as molar product yield per gram of catalyst.

S6 - Determination of Maximum Temperature Conditions by GC

Figure S6.1 shows the *in-situ* GC rig used. Pre-calcined, pelletized catalyst samples (0.1 g) were loaded into a quartz reactor, secured with quartz wool, and aligned in a tube furnace. Temperature was regulated by a thermocouple placed within the catalyst bed. Gas feeds were regulated by mass flow controllers. Temperature studies were performed by passing He, O_2 or 1:1 mixtures thereof through a saturator at 2 °C containing methanol or 1:1 methanol:water (as indicated in Table S6.1), such that the total flow rate was 50 sccm. The vapour was passed over the catalyst surface while heating from 25 to 400 °C (2 °C/min), with gas sampling and analysis by GC at 25 °C intervals.

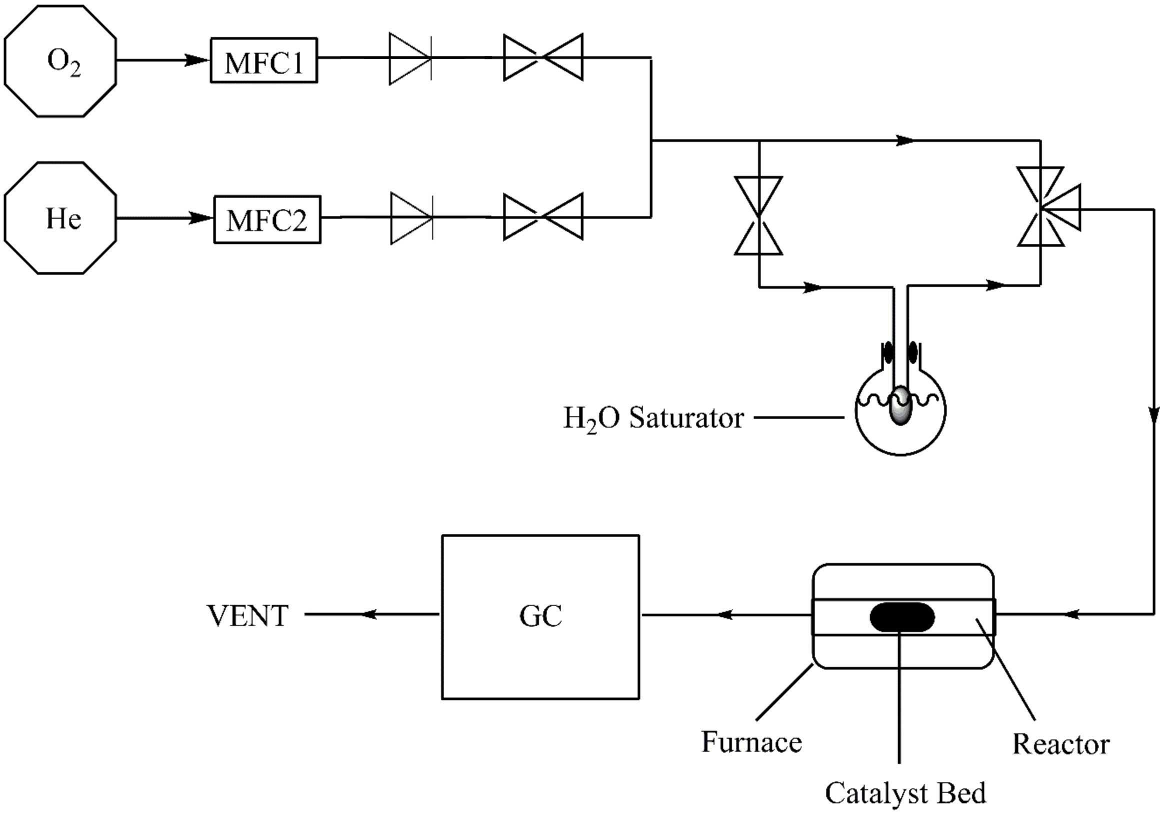


Fig. S6.1 - *In-situ* gas phase GC rig for catalyst temperature profiling.

Analysis was performed using a PerkinElmer Clarus 500 GC, equipped with a TCD and a Chromosorb 102 column (3 m x 2 mm, 80/100 mesh). Samples were collected for 30 seconds and introduced at 150 °C. The column was held at 30 °C for 5 mins, heated from 30 to 200 °C (20 °C/min) and finally held for 30 mins. Carrier gas pressure was constant at 20 psig, total flow rate during sampling was 50 sccm. Products were identified by retention time matching with samples of known gases. Product volumes were quantified by calibration curve. The results of temperature profiling are shown in Table S6.1.

Table S6.1 - Temperature profiles of methanol combustion over Na-/Cu-ZSM-5

Gas Feed	Catalyst	(a)Max. Temp. (°C)	(b)Outlet Composition (%)			
			CH_3OH	CO_2	DME	(c)Other
He, CH_3OH	Na-ZSM-5	250	88.3	0.1	1	11.6
He, CH_3OH	Cu-ZSM-5	200	99.5	-	0.5	-
He, O_2, CH_3OH	Na-ZSM-5	300	96.1	1.30	0.40	2.20
He, O_2, CH_3OH	Cu-ZSM-5	200	98.8	0.02	0.75	0.43
He, O_2, CH_3OH, H_2O	Cu-ZSM-5	225	95.4	4.60	-	0.02

(a)Defined as the temperature at which CO_2 or DME was first observed by GC during heating from 25-400 °C. (b)The composition of methanol and products detected at the reactor outlet. (c)Other components include $H_2O_{(g)}$ and further oxidation products.

In this case, the maximum process temperature was defined as the point below which the introduction of oxidant, methane then water to the catalyst would not be expected to lead to destruction of the desired product methanol. Comparing the maximum process temperature with both Na-ZSM-5 and Cu-ZSM-5 clearly shows the promotion of methanol combustion in the latter case, leading to a lower recommended maximum process temperature of approximately 200 to 250 °C over Cu-ZSM-5. DME was also observed as a secondary product in the absence of water, formed by catalytic dehydration of methanol. For the purposes of this investigation, methanol was the desired product, therefore the recommended maximum temperature also reflects the point below which DME was not expected to form.

S7 - Regeneration of UV-vis Features under NO

Sequential pulsing experiments on Cu-ZSM-5 were performed in the UV-vis rig shown in Figure S3.1, using NO, CH_4 and steam. Steam was applied by replacing the cold trap with a H_2O saturator maintained at 25 °C, using Ar as carrier gas. Tubing was heated to prevent condensation of steam prior to contact with the catalyst bed. The following conditions were applied in chronological order:

- pre-reduction at 500 °C in Ar (50 sccm) for 3 hours,
- activation in NO (25 sccm, 1% in Ar) for 1.5 hours,
- deactivation with steam (2% in Ar) for 1.5 hours,
- reactivation in NO as previous,
- reaction with CH_4 (50 sccm, 1% in Ar) for 1 hour,
- product extraction with steam as previous,
- reactivation in NO as previous.

A constant temperature of 150 °C was maintained during each stage. Between stages, the reactor was cooled to ambient temperature and flushed with Ar before analysis by UV-vis.

The apparent regeneration of the active core species during interaction with NO, regardless of previous treatment with methane and steam, was investigated further by transmission IR. Untreated Cu-ZSM-5 samples (20 mg) were pressed into self-supporting wafers and placed in a gas exchange IR cell. The samples were outgassed at 150 °C for 30 mins to remove surface contaminants, notably this is below the temperature at which water was expected to fully desorb from the zeolite surface. The catalysts were then exposed to NO (1% in Ar, 25 sccm) at 40 °C and the surface analysed by IR, the results are shown in Figure S7.1 below. Prior to IR analysis, a dry KBr disc was scanned to provide the instrument baseline. Spectra were recorded from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and were the result of 128 scans. Normalisation was performed to the zeolite overtone centred at 2000 cm^{-1}.

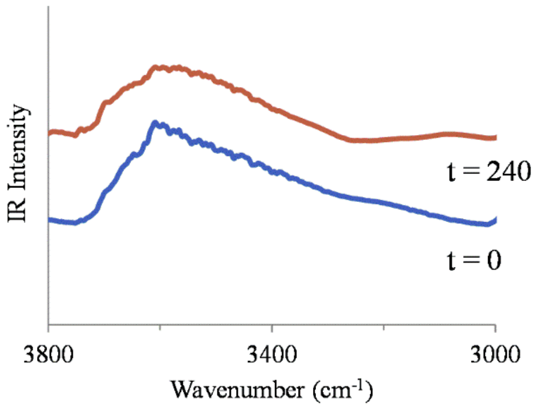


Fig. S7.1 - Transmission IR spectra of Cu-ZSM-5 during NO adsorption (1% in Ar, 25 sccm) at 40 °C. Water region absorbance shown to decrease after 4 hours of treatment.

The results support the observed regeneration of active core species by UV-vis during contact with NO, which occurred regardless of previous treatment of the catalyst with methane followed by steam. This indicates strong competitive chemisorption of NO displacing water from the catalyst surface during treatment.

The mechanism of copper core activation is linked to the decomposition of both NO and N_2O, as discussed by Iglesia et al. [16]. These processes are summarised in Figure S7.2.

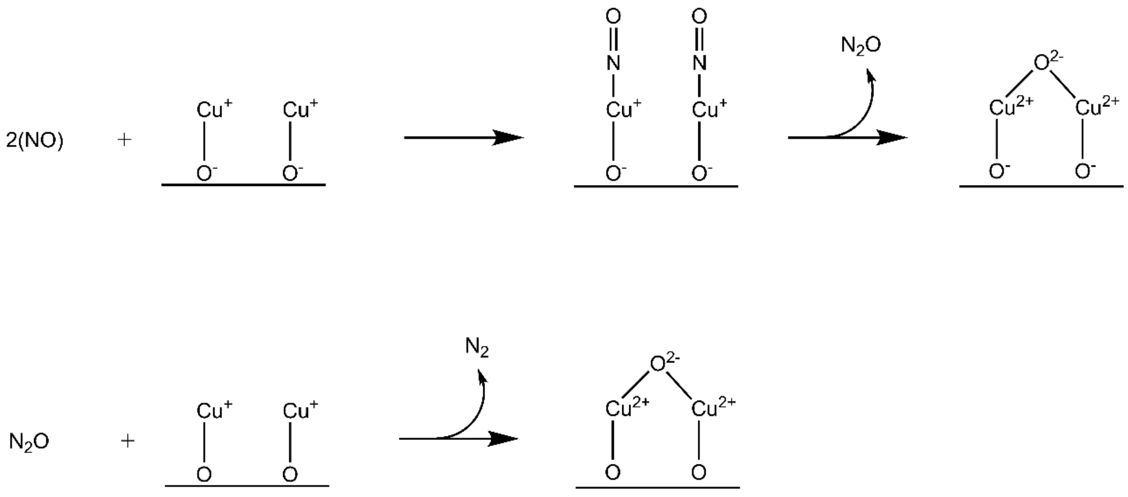
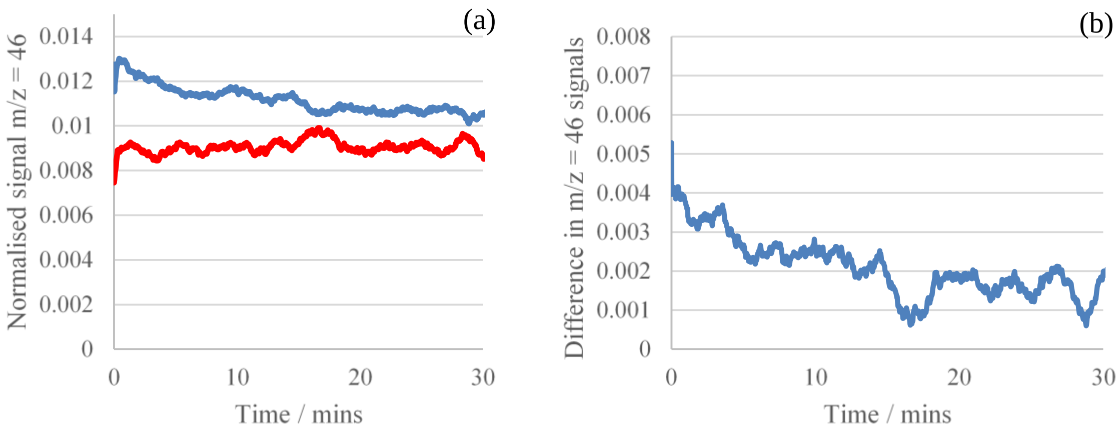


Fig. S7.2 - Activation profile of NO and N_2O showing adsorption and dissociation on Cu-ZSM-5 accompanied by formation of the active core species.

To confirm that this mechanism was also occurring here, a similar rig to that shown in Figure S5.1 was used to heat Cu-ZSM-5 under argon to 150 °C (10 °C/min). A pre-mixed feed of

^{15}NO/Kr/Ar (20/10/20 sccm) was prepared and vented before being introduced to the reactor and MS. Isotopically labelled NO was used to aid product identification, as the masses of products from unlabelled NO, (m/z = 28 and 44 for N_2 and N_2O respectively) are shared with CO and CO_2. The oxidant mixture was passed over the catalyst for 1 hour and analysed using a Hiden HPR 20 MS. To determine the adsorption and reaction occurring on the catalyst the same gas mixture was passed through an empty reactor. The following traces (m/z in parenthesis) were monitored: H_2O (17), $^{14/14}N_2$ (28), $^{15/15}N_2$ (30), ^{14}NO (30), ^{15}NO (31), $^{14/14}N_2O$ (44), $^{15/15}N_2O$ (46), Kr (84). Relative SEM for traces m/z = 30 and 46 was 0.1, with all others being 1.0. Raw mass spectra were baseline corrected and normalised using the Kr trace as internal standard. Formation of $^{15/15}N_2O$ (m/z=46) was confirmed by an increase in signal m/z = 46 as shown in figure S7.3 (a) and (b). N_2O was the minor component of nitrogen containing species with 87% being $^{15/15}N_2$, taken at maximum concentration of each species and using a relative response of 1.0 for N_2 and 0.71 for N_2O (A. Goguet, D. Schweich, J-P Candy, *J. Catal.*, 2003, **220**, 280-290) as shown by the increase in the m/z=30 signal. Iglesia et al. [16] have shown that N_2O can be reduced to give N_2 at the dicopper site at higher temperatures, also observed in this work. However, as no core was observed on UV-vis analysis when N_2O was in contact with Cu-ZSM-5 at 150 °C, formation of $^{15/15}N_2$ is proposed to occur at other sites.



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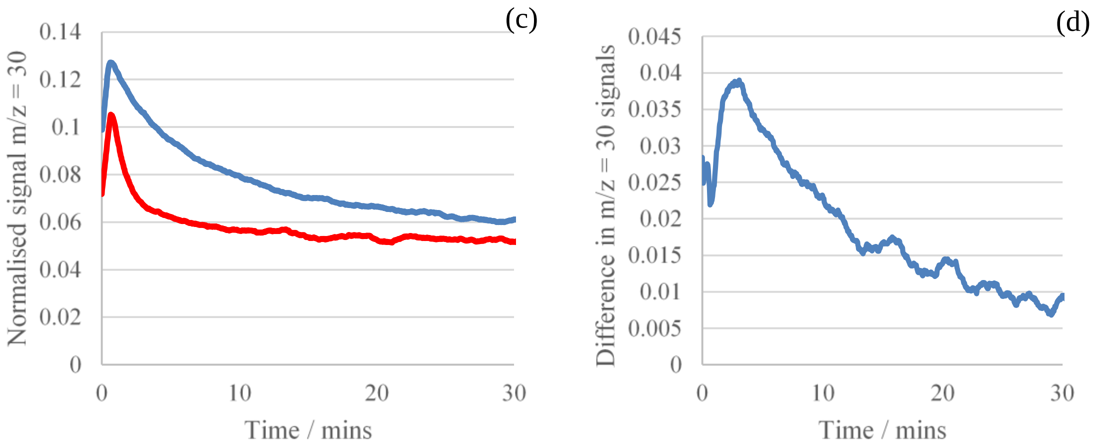

Fig. S7.3 – *In-situ* mass spectrometry following $^{15/15}N_2O$ and $^{15/15}N_2$ traces (m/z = 46 and 30 respectively). (a) and (c): the red line shows the trace from the mixed gas stream when passed through an empty reactor and the blue line shows the trace obtained when the mixed gas stream was passed over Cu-ZSM-5. (b) and (d): the difference in the signals obtained from an empty reactor and that containing Cu-ZSM-5.

S8 - Reaction Profiles and Recyclability of Cu-ZSM-5

Having established activity for partial methane oxidation using Cu-ZSM-5 activated by NO or N_2O, the recyclability of the process with each oxidant was investigated.

Figure S8.1 shows the raw mass spectra obtained during two complete cycles of the NO activated process isothermally at 150 °C. The method was as described in S5 including activation (a), contact with methane (b) and then steam (c). Methanol was observed as the sole product during contact with steam. Following product extraction and while maintaining a temperature of 150 °C, dry Ar (50 sccm) was passed for 30 mins to eliminate excess water from the gas stream. During Ar purging, a pre-mixed feed of NO/Kr/Ar (25/10/15 sccm) was prepared and vented for 15 mins, then introduced to the reactor and MS directly at 150 °C, see Figure S8.1 (d). This was intended to remove adsorbed water and reactivate the catalyst.

The observation of water desorption during contact of the spent catalyst with NO for a second time, together with the UV-vis spectra obtained under analogous conditions, indicates successful catalyst reactivation directly at 150 °C. This was confirmed by repeated contact with methane followed by steam, which yielded methanol in a second reaction cycle, see Fig. S8.1 (e). This offers the possibility of operating a continuous, isothermal, batch type process. The raw spectra obtained throughout catalytic testing indicated no products of combustion, implying total recovery of the product.

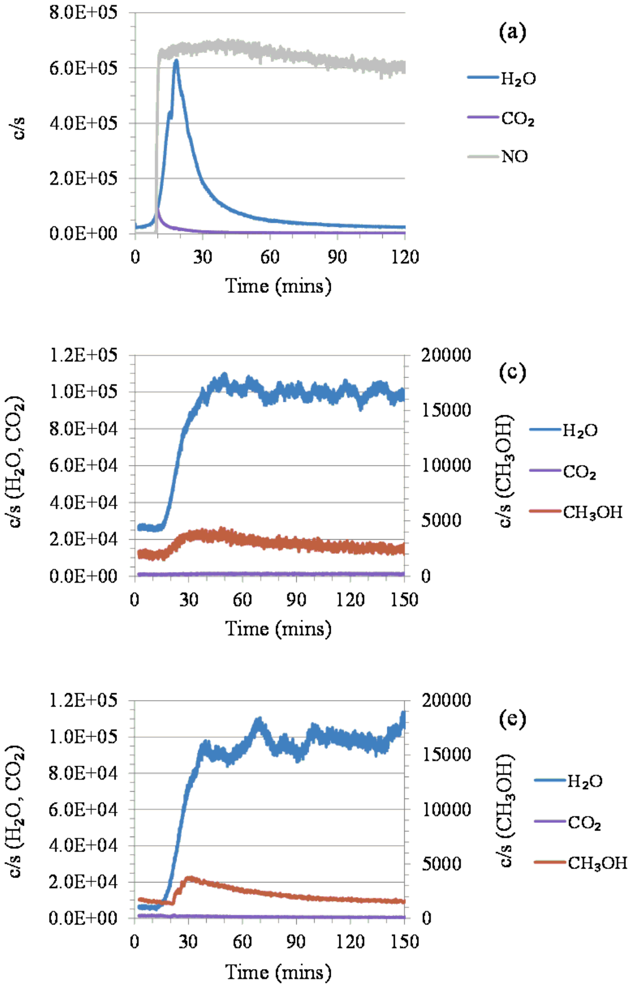

Fig. S8.1 - *In-situ* mass spectrometry following CH_4, H_2O, NO, CH_3O^+ and CO_2 traces (m/z = 15, 18, 30, 31 and 44 respectively): (a) activation in NO; (b) reaction with methane; (c) extraction with steam; (d) 2nd cycle activation in NO; (e) 2nd cycle extraction with steam. A constant temperature of 150 °C was maintained throughout.

The same sample of Cu-ZSM-5 was further tested using N_2O as oxidant, using the method discussed in S5. Activation was first performed at 300 °C, followed by contact with methane and steam extraction. The process was then repeated with activation in N_2O at 200 °C. The resulting mass spectra are shown in Figure S8.2.

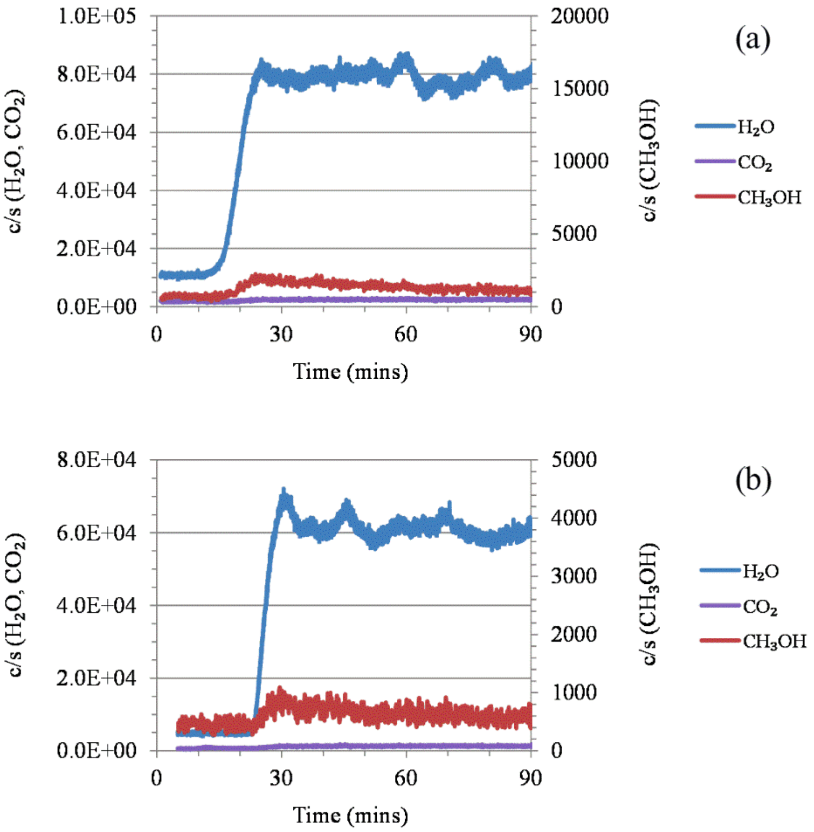

Fig. S8.2 - *In-situ* mass spectrometry following H_2O, CH_3O^+ and CO_2 traces (m/z = 18, 31 and 44 respectively), showing product extraction with steam after: (a) activation in N_2O at 300 °C; (b) activation in N_2O at 200 °C.

Activation in N_2O at both 200 and 300 °C led to the observation of methanol, however none was observed at 175 °C. The minimum temperature possible using N_2O was therefore determined to be 200 °C during activation, followed by 150 °C for reaction and product extraction. The continued use of a single sample throughout this investigation attests to the recyclability of the process in either NO or N_2O.

S9 - Temperature Profiles using Cu-ZSM-5 and Similar Systems from the Literature

With the results obtained, Figure S9.1 therefore shows the proposed temperature profiles developed in this work, with the combustion of methanol indicated. A typical profile for the classical oxidation pathway using O_2 is also shown for comparison.

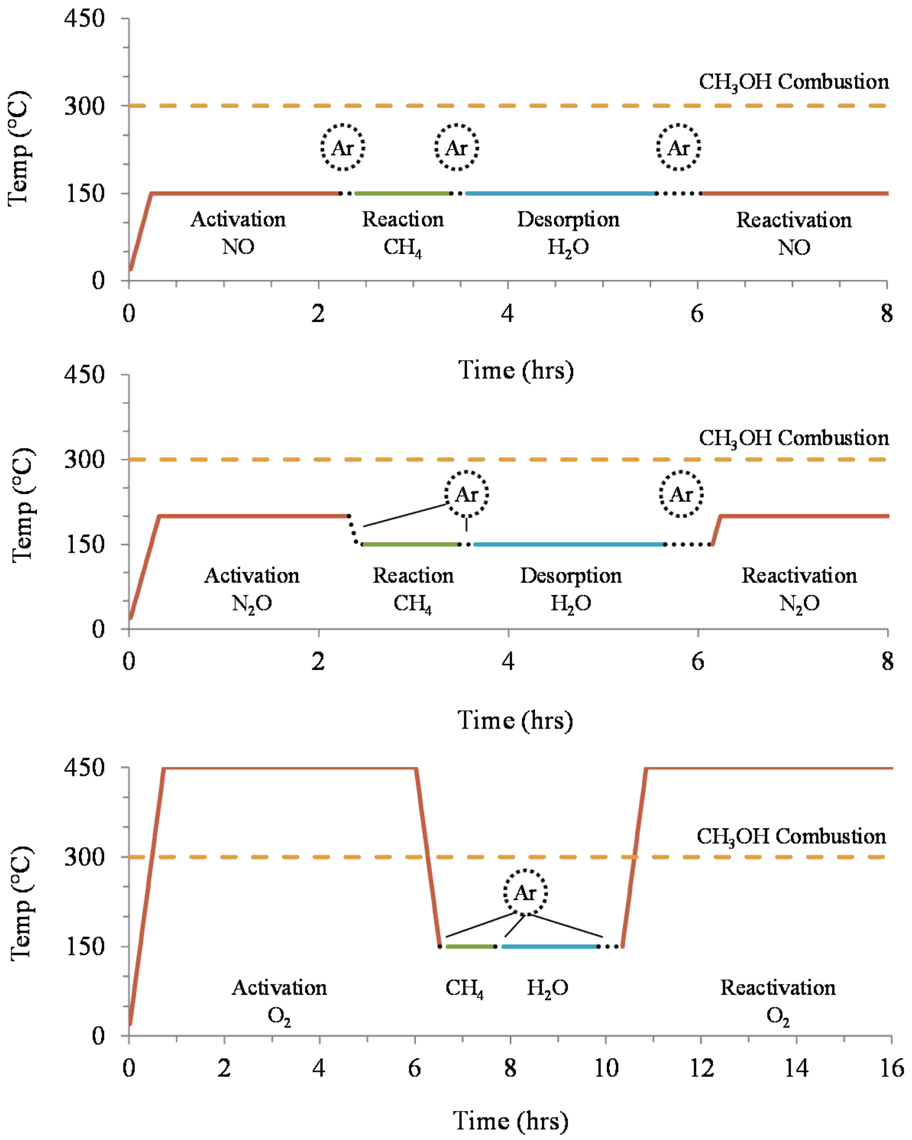

Fig. S9.1 - Reaction profiles of partial methane oxidation on Cu-ZSM-5 yielding methanol, indicating the maximum temperature step: (a) activation in NO at 150 °C; (b) activation in N_2O at 200 °C; (c) activation in O_2 at 450 °C. One complete cycle is shown, including conditions required for reactivation.

Numerous examples of partial methane oxidation over various catalytic systems exist in the literature. Several of these are presented in Table S9.1 together with the present work under investigation.

Table S9.1 - Comparison of catalytic systems for partial methane oxidation

Catalyst System	CH$_3$OH		CH$_3$OH Extraction	TOF(b) (h^{-1})	Ref.
	µmolg^{-1}	% Sel.			
Cu-ZSM-5 / O$_2$	9(a)	98	Aq. 20 °C	-	[14]
Cu-MOR / O$_2$	13	98	Steam 150 °C	-	[10]
Fe-ZSM-5 / N$_2$O	-	100	Aq. 20 °C	-	[17]
Fe/Cu-silicalite-1 H$_2$O$_2$ @ 50 °C	6237	93	Extraction to solvent(c)	70	[12]
Cu-ZSM-5 NO @ 150 °C	0.629	98(d)	Steam 150 °C	0.043	this work
Cu-ZSM-5 N$_2$O @ 300 °C	0.690	98	Steam 150 °C	0.047	this work
Cu-ZSM-5 N$_2$O @ 200 °C	0.137	98	Steam 150 °C	0.009	this work

(a)Based on yield using a catalyst with approximately equivalent Cu wt.% to that presented here. (b)TOF = (mol product / mol metal * reaction time). Assuming approximately 5% Cu is catalytically active, [14] reaction time is defined as the contact time with methane (1 h). (c)Separation procedure required to isolate product. (d)Reaction with CH$_4$ occurs regardless of the activation method, the defined yield of 98% is therefore analogous to gas-phase Cu-ZSM-5 based systems in the literature.

Data shown in Table S9.1, describing systems which do not demonstrate a continuous process of activation, reaction and regeneration of the catalyst are not defined here as catalytic and are not presented with relevant TOF values. This applies to the classic O$_2$ activation pathway on Cu-ZSM-5, which involves removal of the catalyst from the reactor followed by aqueous product extraction. Replacing aqueous extraction with steam desorption again is not considered continuous, due to the high temperature treatment required before the catalyst can be reactivated.

In contrast, the aqueous H$_2$O$_2$ system does demonstrate a catalytic cycle and appreciable turnover. However, the separation of products cannot occur in a continuous manner and the system is operated in a batch reactor. The work presented herein demonstrates a continuous isothermal process, in the case of NO activation. Products may be readily extracted and separated, allowing operation entirely in the gas phase. By demonstrating the possibility to recycle the catalyst in situ with further exposure to NO, this qualifies as a gas phase catalytic system, with the additional advantage of simple product extraction. The limitation with the work presented here is lower yields than can be typically obtained through other processes.