Continuous selective oxidation of methane to methanol on H⁺-Ferrierite having a sheet-like morphology

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SI. 1 Methods and Materials

SI.1.1 Catalyst Synthesis and Preparation

Com-Ferrierite: NH₄⁺-Ferrierite was obtained from Alfa Aesar (45884, Si/Al=10). H⁺-Ferrierite was obtained following heat treatment of NH₄⁺-Ferrierite at 550 °C for 5 h in a static oven using a heating rate of 2 °C min⁻¹.

Nano-FER zeolite was synthesized using hydrothermal method reported by Wang et al.¹. The synthesis gel has a molar composition of 1 SiO₂: 0.0314 Al₂O₃: 0.066 Na₂O: 0.4 piperidine: 17 H₂O: 0.01 CTABr. With the help of CTABr (Cetyltrimethylammonium bromide, Sigma, 98% purity) and piperidine (Acros, 99% purity) 12.52 g of Ludox HS-40 (Aldrich), 0.485 g of sodium aluminate (Sigma Aldrich), 0.158 g of NaOH (Merck, 99%), 18 g of DI H₂O and 0.17 g CTABr were stirred for 30 minutes at 25 °C. It was then transferred to a 35 mL Teflon-lined autoclave and maintained at 110 °C for 36 hours with a rotating speed of 45 rpm in the tumbling oven. After 36 h, the gel was quenched and 2.83 g of piperidine was added to the mixture. The resulting mixture was kept at 150°C for 132 more hours at a rotating speed of 60 rpm. The final mixture was separated at 4000 rpm using a centrifuge and washed with DI water until a pH value of 7 was obtained. The recovered solid was dried at 60 °C overnight. Samples of Nano-Na⁺-FER were calcined at 550 °C for 5 hours under 40 scem air flow.

 NH_4^+ -exchange was performed using 1 M NH_4NO_3 solution (NH_4NO_3 , Sigma Aldrich, 99%) at a basis of 100 mL solution per gram of zeolite. The solution was stirred for 3 hours at 80 °C for ion-exchange. 3 hours later, the zeolites were vacuum filtered using cellulose acetate membranes having 200 nm pore size, washed using deionized H_2O , and dried at 80 °C under static conditions for one hour. This exchange procedure was repeated under the same conditions using the exchanged zeolite. Finally, the heat treatment was performed at 550 °C for 5 h in a static oven using a heating rate of 2 °C min⁻¹ to obtain Nano-H⁺-FER.

Additional heat treatment was applied to Nano-H⁺-FER at 750 °C, 800 °C or 850 °C for 5 h in a static oven using a heating rate of 5 °C min⁻¹ to obtain Nano-H⁺-FER-750, Nano-H⁺-FER-800, and Nano-H⁺-FER-850, respectively.

Cu²⁺-exchange was made by exchanging the H⁺-form of the zeolites in copper (II) acetate solution at different temperatures. 1 g of H⁺-zeolite was treated in 250 mL of aqueous solutions containing copper (II) acetate monohydrate (Merck, 99% by weight) at varying concentrations (0.0002M–0.002M). The exchange procedure was performed for 2.5 to 6 h at 18 °C (see Table S2), depending on the desired extent of exchange. After the exchange, obtained Cu²⁺-zeolites were filtered or centrifuged, washed using 500 mL of deionized water, and dried overnight at 80 °C.

Pyridine adsorption prior to catalytic activity measurements was performed at 150 °C. Firstly, Nano-H⁺-FER or Nano-H⁺-FER-850 was dried at 350 °C for 2 hours under vacuum. After cooling to 150 °C, pyridine (Sigma Aldrich, 99%) was added to the zeolite dropwise until all zeolite was immersed. Then, vacuum was applied while increasing the temperature to 325 °C using a heating rate of 5 °C min⁻¹. The sample was further evacuated at 325 °C for half an hour before carrying it to the reactor.

SI.1.2 Characterization Methods

 N_2 physisorption experiments were performed using a surface area and pore volume analyzer (Micromeritics Tristar II 3020) located in the Chemical Engineering Department at METU. Samples were

degassed in a vacuum set-up (Micromeritics VacPrep 061) at 300 °C for 6 hours under 150 μ mHg vacuum conditions before N₂ adsorption studies. N₂ adsorption and desorption experiments were carried out at relative pressures (P/P₀) ranging from 10⁻⁵ to 0.98 and a constant temperature of -196 °C. The statistical thickness, t-plot, method was applied to calculate the micropore volumes. The Barret-Joyner-Halenda (BJH) adsorption model was used to calculate the pore size distributions. The mesopore volume was calculated by subtracting the t-plot micropore volume from the single point pore volume at P/P₀ = 0.98.

Powder X-Ray Diffraction (XRD) patterns were obtained at METU Central Laboratory using a Rigaku Miniflex X-ray diffractometer. A scan rate of 5° min⁻¹ was employed within the 2 θ range of 2–50°. Cu K α cathode tube (λ = 1.5418 Å) operated at 40 kV and 15 mA. XRD analysis was performed following the calcination of synthesized or ion-exchanged materials.

The elemental compositions of the prepared samples were analyzed using an inductively coupled plasmaoptical emission spectrometer (Perkin Elmer Optime4300DV, ICP-OES) located at METU Central Laboratory. The samples were initially dissolved in an HF/HNO₃ solution overnight.

Scanning Electron Microscopy (SEM) was used to analyze the morphology of the prepared zeolites. SEM analysis was conducted at METU Chemical Engineering Department utilizing a TESCAN VEGA3 at 15–20 kV. Prior to analysis, the calcined samples were coated with a combination of Pd and Au. Transmission Electron Microscopy (TEM) analysis was performed at Bayburt University Central Laboratory using FEI TALOS F200S TEM (200 kV).

²⁷Al MAS-NMR spectra of Nano-Na⁺-FER and Micro-NH₄⁺-FER were obtained using JEOL NMR Spectrometer UltrashieldTM 500 MHz equipped with 5 mm standard probe located at Eskişehir Osmangazi University Central Research Laboratory. AlNO₃'s NMR spectrum was taken before each sample as a standard. The analysis was obtained with a relaxation time of 5 second and a spin rate of 6kHz.

SI.1.2.1 Diffusive Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

DRIFTS experiments were performed using a Nicolet IS50 FTIR spectrometer equipped with a liquid nitrogen-cooled MCT detector, a KBr beam splitter, and an in-situ reaction cell (Harricks – Praying Mantis). Powder catalysts were finely ground and loaded into the sample chamber. Prior to each experiment, the cell was flushed with 30 sccm Ar at room temperature to sweep air. Background subtraction was performed using OMNIC 9 software. Three types of DRIFTS experiments were performed in this study.

i) Dehydration DRIFTS

To examine the effect of dehydration, background spectrum was first obtained over KBr in the cell at 25 °C after a pretreatment step at 110 °C to remove moisture. Then, sample was loaded in the cell and was subjected to dehydration at 450 °C for 1 h. Pre- and post-dehydration spectra were obtained at 25 °C and subtracted from KBr spectrum.

ii) DRIFTS of Adsorbed Pyridine

Following the same dehydration procedure at 450 °C under 30 sccm Ar, the sample was cooled stepwise to 150 °C while collecting background spectra at 450 °C, 350 °C, and 250 °C. Pyridine vapor was introduced to the Ar flow through a liquid pyridine bubbler at room temperature. After the background spectrum was obtained at 150 °C, pyridine vapor in Ar was introduced to the reaction cell for 1 h. The flow was then switched to Ar and weakly bound species were removed from the cell for 15 min. Desorption spectra were collected and subtracted from their respective background spectra obtained at the same temperature before

the pyridine adsorption step. To facilitate diffusion of pyridine into zeolite, adsorption was also performed at 250 °C for Nano-FER samples.

iii) DRIFTS of Adsorbed N₂O

After sweeping air from the reaction cell, temperature was increased to 450 °C at a ramp rate of 10 °C/min and kept at 450 °C for one hour for dehydration under 30 sccm Ar flow. The temperature was then reduced to 25 °C, and a background spectrum was collected. Subsequently, N_2O was introduced to the cell at the same flow rate for 30 min for adsorption. After the adsorption, the gas flow was switched back to Ar and desorption spectra were collected with respect to time.

SI.1.3 Computational Details

Periodic density functional theory (DFT) simulations were performed using the Vienna Ab initio Simulation Package (VASP)² employing the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional³ within the projector augmented-wave (PAW) framework⁴. A plane-wave energy cutoff of 500 eV was applied in all calculations. Structural optimizations were carried out by relaxing all the atoms in the supercell until the residual atomic forces were below 0.01 eV/Å, with an electronic self-consistent field (SCF) convergence threshold of 1×10^{-6} eV.

Grimme's D3 dispersion correction⁵ was included to account for long-range van der Waals interactions. Brillouin zone sampling was performed using the Monkhorst–Pack scheme, with a $3 \times 2 \times 4$ k-point grid for the FER unit cell. A wider supercell was also needed to represent the cage structure. This model was prepared by repeating the single unit cell two times in z-direction. A 3x2x2 k-point grid was employed for this structure. The optimized lattice constants of the FER framework were determined using the Murnaghan equation of state, yielding a = 19.2409 Å, b = 14.4143 Å, c = 7.5949 Å, and $\alpha = \beta = \gamma = 90^{\circ}$.

The gas-phase N₂O molecule was optimized in a large periodic box using only the Γ -point (1×1×1) to avoid spurious interactions, ensuring a minimum intermolecular separation of 13 Å.

To simulate surface reactivity, two slab models were constructed by cleaving the FER crystal and introducing vacuum regions. FER(010) slab was generated by cutting the crystal along the (010) plane and adding 15 Å of vacuum along the *y*-direction. This slab preserves the stoichiometry of bulk FER (SiO₂) and retains the full unit cell in the *x* and *z* directions. A $2 \times 1 \times 4$ Monkhorst–Pack grid was used. The top three atomic layers were relaxed, while the remaining layers were kept fixed to mimic bulk-like behavior. Similarly FER (100) slab was prepared by cleaving along the (100) plane, with 15 Å of vacuum added in the *x*-direction. In this case, a $1 \times 2 \times 4$ k-point grid was used. Again, only the top three atomic layers were relaxed, while the lower portion of the slab was frozen. Necessary dipole corrections we included for the asymmetric usage of slabs.

The adsorption energy of N₂O on FER was computed using Equation (S1):

$$\Delta E_{ads} = E_{N_2O/FER} - (E_{N_2O(g)} + E_{FER})$$
(S1)

where $E_{N_2O/FER}$ is the total energy of the adsorbed system, $E_{N_2O(g)}$ is the energy of the isolated N₂O molecule in the gas phase, and E_{FER} is the energy of the FER structure.

SI.1.4 Reaction System and Procedure

The methane to methanol conversion reaction was carried out in a quartz tubular reactor having an inner diameter of 7 mm and an outer diameter of 9 mm. The reactor was mounted in a furnace, and the furnace temperature was controlled using a temperature controller with a thermocouple placed near the center of the catalyst bed outside the reactor. Zeolite powder was pelletized at 60 psi pressure for 4 minutes and sieved using a sieve to a particle size of $250-500 \,\mu\text{m}$. The zeolite bed was fixed in the reactor with the help of glass wool. The reactor was then placed in the middle of the furnace heating zone. The catalyst bed length was kept at approximately 0.9–1.3 cm. The flow rate of helium (Hatgaz, 99.999% purity), nitrous oxide (Hatgaz, 99%) and methane (Hatgaz, 99.995%) gases were controlled with separate mass flow controllers (ALICAT, MC-100SSCM-D). H₂O was introduced into the feed gas stream by directing the gas stream into a bubbler of deionized water maintained at 42 °C, resulting in a pressure of 8 kPa H₂O. All gas lines were heated to at least 60 °C to prevent any condensation. The effluent stream from the reactor was directed to a gas chromatograph (GC, Agilent 7820A) equipped with a Pora-Plot Q column (CP7554, 25 m, 0.53 mm, 20 µm) and a CP-Molsieve 5Å column (CP7538, 25 m, 0.53 mm, 50 µm). Gas chromatograph (GC) was used for the quantification of methanol and other gases produced. The thermal conductivity detector and flame ionization detector were operated simultaneously to detect and quantify the products. Qualitative and quantitative analysis of N₂, CO, CO₂, N₂O, CH₄, dimethyl ether (DME), C₂H₆, C₂H₄, C₃H₆, C₃H₄, and C₄+ was performed using single-point calibration of a standard gas sample. Methanol calibration was performed by saturating inert He with methanol vapor at 25 °C or 0 °C.

Approximately 0.3 g (or 0.1 g) of hydrated Cu-zeolite having a particle size of 250–500 μ m was placed in the quartz reactor. 100 cm³ min⁻¹ He was used to heat the catalyst to the reaction temperature using a heating rate of 5 °C min⁻¹. At the reaction temperature, the feed mixture was introduced to the reactor and chromatogram injections were started. During the reaction, the reaction products were sent to the gas chromatograph at intervals of 21 minutes. The feed composition was 40 mol% CH₄, 15% N₂O, 0-11% H₂O and balance He. As the temperature increased, the partial pressure of H₂O varied accordingly. For the reaction system, GHSV was 20000 mL g⁻¹ h⁻¹ or 60000 mL g⁻¹ h⁻¹.

The previously established setup was used to regenerate the catalyst and to determine the coke amount. For the regeneration, dry air (Hatgaz, 99.99%) flow rate was set to75 sccm and the spent catalyst was heat treated to 550 °C for 2 h using a heating rate of 5 °C min⁻¹. The effluent CO_2 concentration was measured every 7 minutes using a gas chromatograph (Agilent 7820A). The total CO_2 amount was then computed to determine the overall coke amount. The overall coke amount was normalized using the total reaction time to calculate the coke generation rate. The computed coke rate was also considered in methane conversion rate and product selectivity calculations. The equations for selectivity and conversions are provided in Equation S2-S4, and the experimental setup is represented in Figure S1.

$$r_{CH_{4}} = r_{CH_{3}OH} + r_{CO_{2}} + r_{CO} + r_{Coke} + 2 \cdot \sum r_{C_{2}} + 3 \cdot \sum r_{C_{3}} + 4 \cdot \sum r_{C_{4}} \qquad S2$$

$$S_{CH_{3}OH}(\%) = \frac{r_{CH_{3}OH}}{r_{CH_{4}}} \cdot 100\% \qquad \qquad S3$$

$$X_{CH_{4}} = \frac{r_{CH_{4}}}{F_{CH_{4}} \cdot fed/gcat}} \cdot 100\% \qquad \qquad S4$$



Fig. S1. The schematic representation of the reaction set-up

SI.2. Com-H⁺-FER and Nano-H⁺-FER Results

SI.2.1. Characterization Results



Fig. S2. a) SEM and b,c,d) TEM images of Nano-H⁺-FER



Fig. S3. ²⁷Al MAS NMR spectra of a) Com-NH₄⁺-FER b) Nano-H⁺-FER c) Nano-Na⁺-FER d) Nano-H⁺-FER-850 e) Nano-H⁺-FER-800 f) Al-IV and Al-V region for Nano-H⁺-FER-850 g) Al-IV region for Nano-H⁺-FER-800 f) A

Sample	Total Al Distributions (%)			Framework Al (Al ^{IV}) Distributions (%)				
	Al ^{IV}	Al ^v	Al ^{vi}	Distorted Al ^{IV} (40- 50 ppm)	T1 (60- 62 ppm)	T2 (51 ppm)	T3 (54- 56 ppm)	T4 (58- 59 ppm)
Com- NH4 ⁺ -FER	98	0	2	2	24	0	21	53
Nano-H ⁺ - FER	87	0	13	2	2	0	14	82
Nano- Na ⁺ -FER	100	0	0			25	40	35
Nano-H ⁺ - FER-800	79	0	21	15	0	37	36	12
Nano-H ⁺ - FER-850	71	5	24	16	0	31	37	16

Table S1. Framework Al distribution based on deconvolution of ²⁷Al NMR spectra

Table S2. Elemental analysis results using ICP-OES or XRF and textural properties

Sample	Solutio n Cu(II) Molari ty	Ion- excha nge Time	Si/Al	Cu/Al	Langmuir surface area (m² g⁻¹)	V _{total} (cm ³ g ⁻¹)	V _{micro} (cm ³ g ⁻¹)	V _{meso-} macro (cm ³ g ⁻¹)
Com-H ⁺ -FER			8.8		440	0.22	0.13	0.09
Com-Cu-FER	0.003	24 h	8.8	0.02	452	0.21	0.15	0.06
Nano-H ⁺ -FER			11.6		524	0.44	0.13	0.31
Nano-Cu-FER	0.0002	2.5 h	11.9	0.027	488	0.41	0.13	0.28
Nano-H ⁺ -FER-850			11.8		424	0.39	0.10	0.29

SI.2.2. Methanol Formation Activity

				Catalyst			
Rate in µmol g	Com-H ⁺ -	Com-Cu-	Nano-H ⁺ -	Nano-H ⁺ -	Nano-	Nano-H ⁺ -	Nano-
¹ h ⁻¹	FER	FER	FER	FER-Pyr	Cu-	FER-850	H ⁺ -FER-
				·	FER 1		850-Pyr
СН ₃ ОН	1957±30	1748±48	2061±40	1240±36	2191±40	2270±80	2131±75
DME	249±17	102±9	211±12	55.2±0.3	225±7	209±15	90±10
CO	17±6	128±9	13±3	n.d.	6±3	n.d.	n.d
CO ₂	11±1	23±1	17±2	9±2	14±2	6.0 ± 0.6	8±1
C_2H_4	10±2	2±1	16±2	$1.4{\pm}0.1$	4.3±0.3	9.4±0.7	2.1±0.2
C_2H_6	3.6±0.2	0.3 ± 0.2	5±1	1.5 ± 0.1	1.5±0.6	3.3±0.2	1.6 ± 0.1
C_3H_6	6±2	$0.7{\pm}0.1$	8±1	0.6 ± 0.1	1.3 ± 0.2	4.3±0.4	1.1 ± 0.1
C ₃ H ₈	0.9±0.2	0.16 ± 0.04	1.0 ± 0.3	$0.04{\pm}0.01$	$0.2{\pm}0.1$	$0.40{\pm}0.02$	$0.20{\pm}0.01$
C4 total	9±1	0.42 ± 0.03	12±1	n.d.	$1.4{\pm}0.1$	2.9±0.1	n.d.
Coke	271	44	155	316	72	35	68
CH ₄	0.9	0.7	0.9	0.4	0.9	0.8	0.6
Conversion/ %							
N ₂ O	3.3	2.7	3.2		2.7	2.4	1.6
Conversion/ %							
S _{CH3OH} / %	69	81	74(78)*	74(91)*	80	82(83)*	89(91)*
S _{CH3OH+DME} / %	86	90.6	89.2(94)*	80.2(99)*	96	97(98)*	96(99)*
S_{CO+CO2} /%	1	7	1	0.5(0.65)	0.7	0.2	0.3(0.3)
S _{C2-C4} / %	3	0.4	4.2	0.45(0.56)	0.8	1.7	0.4(0.41)
S _{coke} / %	10	2	5.6	19	2.5	1.2	2.8

Table S3. Methane conversion to methanol reaction results obtained at 325 °C and 40.5 kPa CH₄, 15.2 kPa N₂O, 9 kPa H₂O, balance He (~300 mg catalyst, 100 sccm total flow, GHSV= 20000 ml g⁻¹ h⁻¹)

*: Carbon-based selectivity excluding coke formation

n.d.: not determined, concentration below 5 ppm

Table S4. Methane conversion to methanol reaction results obtained at 325 °C and 40.5 kPa CH₄, 15.2 kPa N₂O, 11 kPa H₂O, balance He (~100 mg catalyst, 100 sccm total flow, GHSV= 60000 ml g⁻¹ h⁻¹)

			Catalyst		
Rate in µmol g ⁻¹ h ⁻¹	Com-H ⁺ -	Com-	Nano-H ⁺ -	Nano-	Nano-H ⁺ -
	FER	Cu-	FER	Cu-	FER-850
		FER		FER_1	
СН ₃ ОН	3164±100	2437±82	3355±100	1453±70	3718±72
DME	215±27	159±27	240±19	51±5	280±35
CO	114±50	49±10	120±50	67±30	195±42
CO_2	12±4	16±3	9±2	17±2	9±4
C_2H_4	19±5	6±1	19±4	4.1±0.3	13±1
C_2H_6	6±2	$3.4{\pm}0.5$	7±1	n.d.	5.6 ± 0.7
C_3H_6	5±2	0.5 ± 0.2	5±2	$0.4{\pm}0.1$	5.5 ± 1.0
C_3H_8	0.5±0.2	n.d.	$0.4{\pm}0.2$	n.d.	$0.4{\pm}0.1$
C ₄ total	4.7 ± 0.4	3.2±0.2	4.4 ± 0.6	3.9±0.2	2.1±0.3
Coke	55	30	27	25	44
CH ₄ Conversion/ %	0.4	0.3	0.4	0.2	0.5
N ₂ O Conversion/ %	1.1	0.9	1.0	0.5	1.0
S _{CH3OH} / %	82	85	82(83)	86	81(83)*
S _{CH3OH+DME} / %	93	96	94(95)	92	94(95)*
S _{CO+CO2} / %	3.3	2.3	3.2	5.0	1.1
S _{C2-C4} / %	2.2	1.1	2.2	1.5	0.5
Scoke %	1.4	1.0	0.7	1.5	8

*: Carbon-based selectivity excluding coke formation

n.d.: not determined, concentration below 5 ppm



Fig. S4. Methanol formation rate with respect to time at 325 °C and 40.5 kPa CH₄, 15.2 kPa N₂O, 11 kPa H₂O, balance He (~100 mg catalyst, 100 sccm total flow, GHSV= 60000 ml g⁻¹ h⁻¹)

Rate in µmol g ⁻¹ h ⁻¹	Nano-H ⁺ -	Nano-H ⁺ -	Nano-H ⁺ -
	FER(run1)	FER(run2)	FER(run3)
CH ₃ OH	3278±67	3355±100	3352±100
DME	241±18	240±19	220±20
CO	150±50	120±50	133
CO ₂	8±1	9±2	12±3
C_2H_4	19±4	19±4	19±3
C_2H_6	7±1	7±1	7±2
C ₃ H ₆	6±1	5±2	6±2
C ₃ H ₈	0.5±0.1	$0.4{\pm}0.2$	$0.4{\pm}0.2$
C4 total	4.6±0.5	4.4 ± 0.6	4.2 ± 0.8
Coke	29	27	21
CH ₄ Conversion/ %	0.4	0.4	0.4
N ₂ O Conversion/ %	1.0	1.0	0.9
S _{CH3OH} / %	81(82)*	82(83)*	83(83)*
S _{CH3OH+DME} / %	93(94)*	94(95)*	94(94)*
S _{CO+CO2} / %	4	3.2	3.6
S _{C2-C4} / %	2.3	2.2	2.2
S _{coke} / %	0.8	0.7	0.5

Table S5. Repetition experiments on Nano-H⁺-FER at 325 °C and 40.5 kPa CH₄, 15.2 kPa N₂O, 11 kPa H₂O, balance He (~100 mg catalyst, 100 sccm total flow, GHSV= 60000 ml g⁻¹ h⁻¹)

*: Carbon-based selectivity excluding coke formation

Table S6. Methane conversion to methanol reaction results on additional heat-treated Nano-H⁺-FER obtained at 325 °C and 40.5 kPa CH₄, 15.2 kPa N₂O, 11 kPa H₂O, balance He (~100 mg catalyst, 100 sccm total flow, GHSV= 60000 ml g⁻¹ h⁻¹)

Rate in µmol g ⁻¹ h ⁻¹	Nano-H ⁺ -	Nano-H ⁺ -	Nano-H ⁺ -	Nano-H ⁺ -
	FER	FER-750	FER-800	FER-850
CH ₃ OH	3355±100	2940±110	3298±120	3718±72
DME	240±19	206±25	210±30	280±35
CO	120±50	n.d.	95±50	195±42
CO_2	9±2	9±3	12±3	9±4
C_2H_4	19±4	13±2	12±2	13±1
C_2H_6	7±1	5±1	5±1	5.6±0.7
C_3H_6	5±2	5±2	5±2	5.5 ± 1.0
C ₃ H ₈	$0.4{\pm}0.2$	$0.4{\pm}0.1$	$0.3{\pm}0.1$	$0.4{\pm}0.1$
C4 total	4.4 ± 0.6	2.5 ± 0.5	1.9 ± 0.3	2.1±0.3
Coke	27	44	40	44
CH ₄ Conversion/ %	0.4	0.4	0.4	0.5
N ₂ O Conversion/ %	1.0	0.9	0.9	1.0
S _{CH3OH} /%	82	85	84	81
S _{CH3OH+DME} / %	94	97	95	93
S _{CO+CO2} / %	3.2	0.3	2.7	1.1
S _{C2-C4} / %	2.2	1.7	1.4	0.5
S _{coke} /%	0.7	1.3	1.03	8

SI.3. DRIFTS Analysis and DFT Calculations



Fig. S5. In-situ DRIFT spectra of (a) Nano-H⁺-FER, Nano-Cu-FER, Com-H⁺-FER, and Com-Cu-FER following dehydration at 450 °C for 1 h and (b) Nano-H⁺-FER, Nano-H⁺-FER-850, and Com-H⁺-FER after pyridine adsorption at 150 °C

Due to a much lower intensity of Bronsted acid sites (3600 cm⁻¹ peak, Fig. S5), the adsorbed pyridine at 150 °C did not show as intense absorption peaks for Nano-H⁺-FER or Nano-H⁺-FER-850 when compared to Com-H⁺-FER. The Bronsted acid site and Lewis acid site related peaks at 1544 and 1456 cm⁻¹, respectively were discernible on spectra belonging to Com-H⁺-FER (Fig. S5b and Fig. S6), whereas on spectra of Nano-H⁺-FER or Nano-H⁺-FER-850, absorption peaks at 1595 and 1444 cm⁻¹ (Fig. S5b) is attributed to the hydrogen bonded pyridine on OH defects (SiOH or AlOH groups) (8a, 19b modes respectively)⁶.



Fig. S6. In-situ DRIFT spectra of Com-H⁺-FER and Com-Cu-FER at various desorption temperatures. Pyridine adsorption was performed at 150 °C.

The Bronsted acid sites (1543 cm⁻¹, 1637 cm⁻¹) and Lewis acid sites (1456 cm⁻¹, 1612 cm⁻¹) are mostly preserved on Com-H⁺-FER and for Com-Cu-FER following desorption at 350 °C under inert flow (see Fig. S6).

To be able to ensure pyridine diffusion into all acid sites, pyridine adsorption was performed at 250 °C, instead of 150 °C, for Nano-H⁺-FER and Nano-H⁺-FER-850. It was noted that the adsorbed pyridine amount

was very low, as evidenced by low signal to noise ratio, due to higher adsorption temperature. Even though the peak intensities were low immediately after the adsorption at the same temperature, the absorption peaks at 1544 and 1456 cm⁻¹ were mostly preserved at 350 °C. This ensures pyridine occlusion in FER structure even after desorption at 350 °C. 1637 cm⁻¹, assigned to the pyridinium ion from Bronsted acid sites⁷ is mostly preserved even at 450 °C whereas the intensity of the band at 1612 cm⁻¹ (indicating Lewis acid sites) decreases with temperature.



Fig. S7. In-situ DRIFT spectra of Nano-H⁺-FER and Nano-H⁺-FER-850 following pyridine adsorption at 250 °C and desorption at 250 °C, 350 °C, 450 °C. (No data processing was performed to remove atmospheric water vapor signals.)

	Sample	DRIFTS Frequency	Assignment	DFT (cm ⁻¹)
		(cm ⁻¹)		
О-Н	Com-H ⁺ -FER	3745	External Silanol ⁸	3693, external silanol on bc plane
groups	Com-Cu-FER	3736	Perturbed Silanol	
	Nano-H ⁺ -	3650	Extraframework Al-OH ⁹	3669, surface Al-(O-H) on ac plane, Al T3 position
	FER			3653, surface Al-(O-H) on ac plane, Al T4 position
	Nano-Cu-			3674, surface Al-(O-H) on bc plane
	FER	3600	Bridging Si-(OH)-Al 10 MR ¹⁰	3366 bridging Si-(OH)-Al, Al at T4
				3572 distorted (SiO) ₃ Al(OH)
			DFT (cm ⁻¹)	Optimized Geometry using periodic DFT
T-O-T group	Com-H ⁺ -FER	955	958, Al-O bending, H ⁺ -FER, Site II (8MR, energetically more stable)	calculated : 958 cm ⁻¹ experimental : 955 cm ⁻¹
		906- 860(885)	885, Si-O bending ac and bc plane	computed : 884 cm ⁻¹ experimental : 885 cm ⁻¹

Table S7. DRIFT frequency values of the dehydrated samples and theoretically calculated values

Nano-H ⁺ - FER	971	975, T-O bending, H ⁺ -FER, Site II	calculated : 975 cm ⁻¹ experimental : 971 cm ⁻¹
	885	885, Si-O bending ac and bc plane	
Com-Cu-FER	955	958, Al-O bending, Bronsted, Site II (8MR)	
		960, Si-O bending, Cu, Site I (10MR)	computed : 924 cm-1 (sym) experimental : 912 cm ⁻¹ computed : 863 cm-1 (asym) experimental : 885 cm-1

	912	924, O-Cu bending, Cu, Site I (10MR)	computed experiment computed experiment 55 cm ⁻¹
	906- 860(885)	885, Si-O bending ac and bc plane	
		863, Cu-O bending, Cu, Site I (10MR)	computed
			computed 50 cm ⁻¹ experiment 55 cm ⁻¹
Nano-Cu- FER	971	976, 965, Al-O stretching, Cu, Site II (8MR)	Computeri : 976 cm ⁻¹ (sym) computeri : 955 cm ⁻¹ (asym) experimental : 971 cm ⁻¹

955	960, Al-O bending, Cu, Site I (10MR) 958, Al-O bending, Bronsted, Site II (8MR)	computed experiment computed experiment	30. 5 ⁵	cm ⁻¹
906-866 (885)	863, Cu-O bending, Cu, Site I (10 MR) 885, Si-O bending ac and bc plane	computed experimen computed experimen		50 cm ⁻¹ 55 cm ⁻¹



Fig. S8. Optimized geometries and relative energies (kJ/mol) of Cu-FER using periodic DFT (Si: yellow, Al: light blue, O: red, Cu: dark blue)



Fig. S9. DRIFT spectra of Nano-Cu-FER following N2O adsorption at 25 °C

Table S8: Summary of calculated energies (kJ/mol). ΔE_{2Al} is the relative energy of 2Al replacement with Si atoms, ΔE_{Cu} is the relative energy of Cu addition to 2Al site (kJ mol⁻¹), $\Delta E_{N2O(O)}$ and $\Delta E_{N2O(N)}$ are the N₂O adsorption energies (kJ mol⁻¹) where N₂O binds from O or N end.

Ring	ΔE_{2Al}	ΔE_{Cu}	ΔE_{Cu+2}	$\Delta E_{N2O(}$	v_{as} (cm ⁻¹),	$\Delta E_{N2O(}$	v_{as} (cm ⁻¹),
			Al	N-N-O-Cu)	ν_s (cm ⁻¹)	O-N-N-Cu)	ν_{s} (cm ⁻¹)
Site I (α -site)	+21	+59	+79	-46	2266, 1245	-53	2269,1293
Site II (β -site)	0	0.0	0	-40		-44	2271, 1294
Site III (Y-site)	+5	+62	+67	-39	2259, 1231	-40	
Site IV	+15	+178	+192	-89	2259, 1231	-128	
Distorted				-34	2259, 1275		
tetragonal Al at							
Site II							
Trigonal Al at				-70	2324, 1237		Not favorable
Site II							
Trigonal Al at ac				-60	2298, 1233		
plane(T4)							
Trigonal Al at ac				-53	2304, 1237		
plane(T3)							
Distorted				-31			
tetragonal Al at							
<i>ac</i> plane (T4)							



Fig. S10. Optimized geometries and N₂O adsorption energies (kJ/mol) of Cu-FER using periodic DFT (Si: yellow, Al: light blue, O: red, Cu: dark blue, N: grey)



Fig. S11. Optimized geometries and N₂O adsorption energies (kJ/mol) of H⁺-FER using periodic DFT (Si: yellow, Al: light blue, O: red, N: grey)

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