SUPPLEMENTARY INFORMATION

Dioxygen splitting at room temperature over distant binuclear transition metal centers in zeolites for direct oxidation of methane to methanol

Kinga Mlekodaj[a], Mariia Lemishka[a,b], Stepan Sklenak[a], Jiri Dedecek[a] and Edyta Tabor[a*]

[a] J. Heyrovský Institute of Physical Chemistry of the CAS, v. v. i, Dolejškova 2155/3, 182 23 Prague, Czech Republic

[b] University of Pardubice, Studentská 95, 532 10 Pardubice, Czech Republic

* Corresponding author email address: edyta.tabor@jh-inst.cas.cz

MATERIALS AND METHODS

Sample preparation:

A commercially supplied ferrierite Si/Al 8.6 (Tosoh Corporation, Japan) with a confirmed high crystallinity, exclusivity of framework Al atoms, and adequate adsorption properties; details are provided elsewhere. The commercial NaK-ferrierite zeolite was ion exchanged (3 x 24h, room temperature, 100 ml of solution/1g of zeolite) with 1 M NH_4NO_3, then filtrated, washed by distilled water, and dried at RT to prepare NH_4-ferrierite.[1, 2] The Co(II)-ferrierite sample was prepared by ion exchange of NH_4-ferrierite with 0.05 M solution of $Co(NO_3)_2 \cdot 6H_2O$ at 60 °C, 3 × 24 h, 100 ml of solution/1 g of zeolite. After the ion exchange, the zeolite was thoroughly washed with distilled water and dried in air at RT. Ni(II) and Mn(II) were introduced to ferrierite using the dry impregnation technique. The NH_4-ferrierite sample was granulated (0.3 – 0.6 mm) and dehydrated for 4 h at 120 °C. The impregnation solutions were prepared as followed: 0.20 g of $Ni(NO_3)_2 \cdot 6H_2O$ or 0.14 g of $Mn(NO_3)_2 \cdot 4H_2O$ were dissolved in 1.0 g of water. The impregnation solutions were added drop-wise to NH_4-FER. The samples after impregnation were dried on air for 24 h at RT, and then calcined in air at 450 °C for 4 h.[2, 3] The chemical composition of all studied samples is listed in Table S1.

Table S1. Chemical composition of the M-ferrierite samples.

Sample	Si/Al*	M/Al*	$M(II)_{bare}/Al^{**}$	M(II)**	$M_{bare}(II)^{**}$
				mmol/g	
Ni-FER	8.6	0.28	0.10	0.47	0.17
Mn-FER	8.6	0.22	0.21	0.37	0.35
Co-FER	8.6	0.18	0.15	0.30	0.25

*Results obtained from an XRF analysis.

**Results from a deconvolution of FTIR spectra of M-ferrierites evacuated for 3h at 450°C. The spectra were analyzed in the region 1000-840 cm^{-1} which characterizes the presence of M(II) bare cations. For calculation of the concentration of bare extinction coefficients estimated elsewhere were used.[4]

FTIR spectroscopy experiments:

Infrared spectra were recorded employing a Nicolet 6700 FTIR spectrometer (resolution 2 cm^{-1}, 32 scans/min) equipped with a liquid nitrogen cooled MCT-B detector and KBr windows. The samples in a form of self-supporting pellets (10 mg cm^{-2}) were placed in the cuvette allowing an evacuation and dosing gases. FTIR spectra of the investigated M-ferrierite (M = Ni, Mn, and Co) samples were recorded at RT after the following treatments: (i) an evacuation at 450 °C for 3 h (Manuscript, Figure 2A) under dynamic vacuum at RT; (ii) an evacuation at 450 °C for 3 h, then an interaction at RT with O_2 (10^5 Pa, purity 99.999 %) for 1 h, followed by a 3 min O_2

desorption at RT (Manuscript, Figure 2B); (iii) an evacuation at 450 °C for 3 h, then an interaction at RT with O_2 (10^5 Pa, purity 99.999 %) for 1 h followed by a 3 min O_2 desorption at RT, and subsequent 1 h interaction with CH_4 (10^5 Pa, purity 99.999 %) at RT followed by 3 min evacuation at 220 °C (Manuscript, Figure 2C).

The presence of bare cations in extra-framework sites of the zeolite matrix is reflected as an additional band in the region of T-O-T vibrations ranging from 1000 to 840 cm^{-1}. Conversely, the FTIR spectrum of the H-form of ferrierite does not exhibit any band in the region of T-O-T vibrations. Figure S1 depicts comparison of the FTIR spectra of H-ferrierite and Fe-ferrierite recorded at RT after an evacuation at 450 °C for 3 h.

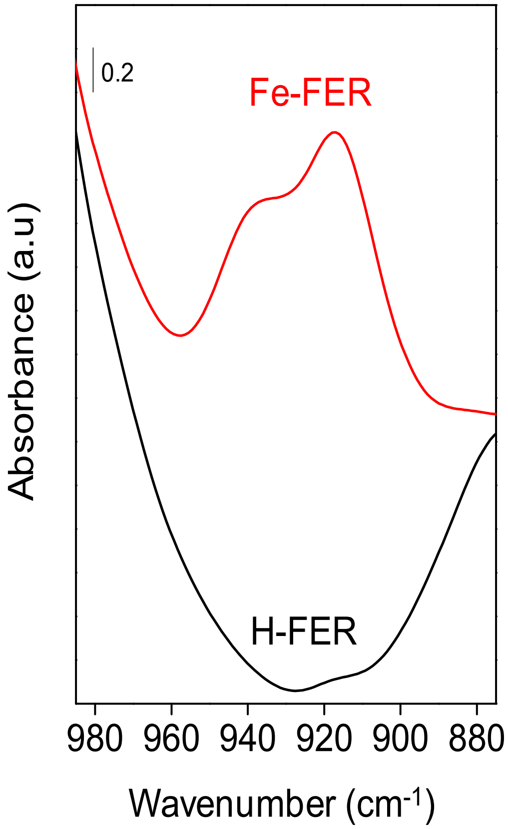

Figure S1. FTIR spectra in the region of T-O-T vibrations of H-ferrierite (black line) and Fe-ferrierite (red line) evacuated at 450 °C for 3h.

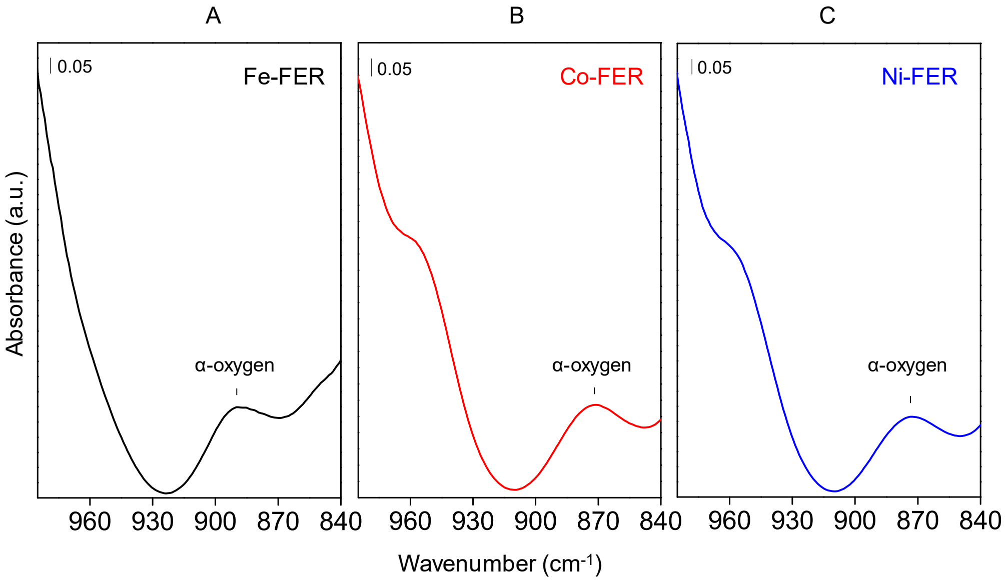

Figure S2. FTIR spectra of Co-ferrierite, Ni-ferrierite, and Fe-ferrierite after an evacuation at 450 °C for 3h followed by an interaction with N_2O at RT for 1h.[4]

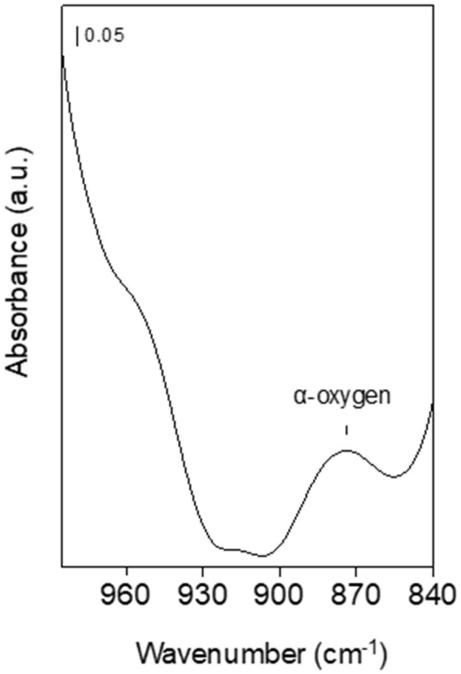

Figure S3. FTIR spectrum of Fe-ferrierite recorded at RT after an evacuation at 450 °C for 3h followed by 1h interaction with O_2 at RT.

Mass spectrometry experiments:

The products of the titration of the α-oxygen formed after an interaction with O_2 at RT with M-ferrierites (M = Ni, Mn, and Co) by methane were monitored by mass spectrometry (Balzers QMG 421 C quadrupole mass spectrometer). The 0.025 g of the M-ferrierite samples were placed in the quartz reactor and activated in an Ar flow (20 mL/min) for 3 h at 450 °C. Subsequently, the samples were treated with O_2 (40 mL/min, purity 99.999 %) at RT for 1 h followed by purging of O_2 excess with Ar (20 mL/min) for 5 min. Finally, the oxidized samples interacted at RT with CH_4 (30 mL/min, purity 99.999 %). The signal with m/z = 31 that relates to methanol was monitored for all the studied M-ferrierite samples. The quantitative analysis was based a calibration using injections of a set of ten different amounts of methanol covering the entire estimated range of the methanol yields.[3] The calibration data for methanol were employed to quantify the yield of produced methanol.

Prior the experiments with M-ferrierite samples (M = Ni, Mn, Co) analogous experiments with the empty reactor, and ferrierite in H-form (without any transition metal ions accommodated in cationic sites, thus without binuclear cationic sites) were performed, and did not reveal presence of any m/z signal that can be assigned to products of methane oxidation.

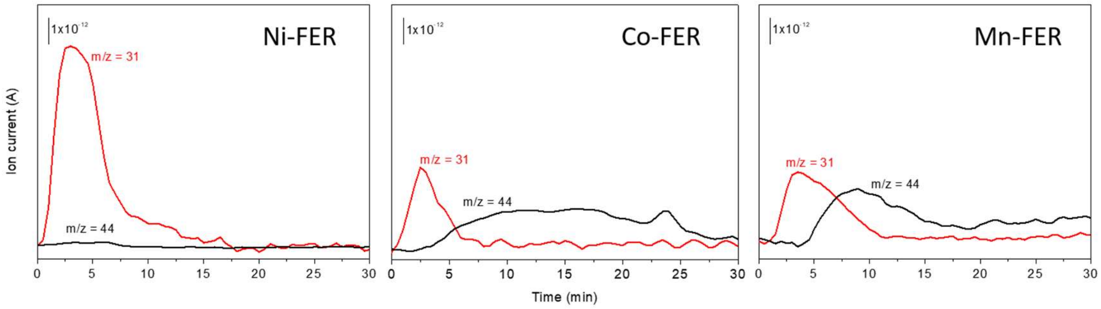

Figure S4. Time dependence of the intensity of the ion current for the signal m/z = 31, reflecting CH_3OH, and m/z = 44 representing CO_2 release after CH_4 oxidation by α-oxygen formed on Ni-, Mn-, Co-ferrierite samples.

Appendix Structural characterization of FER

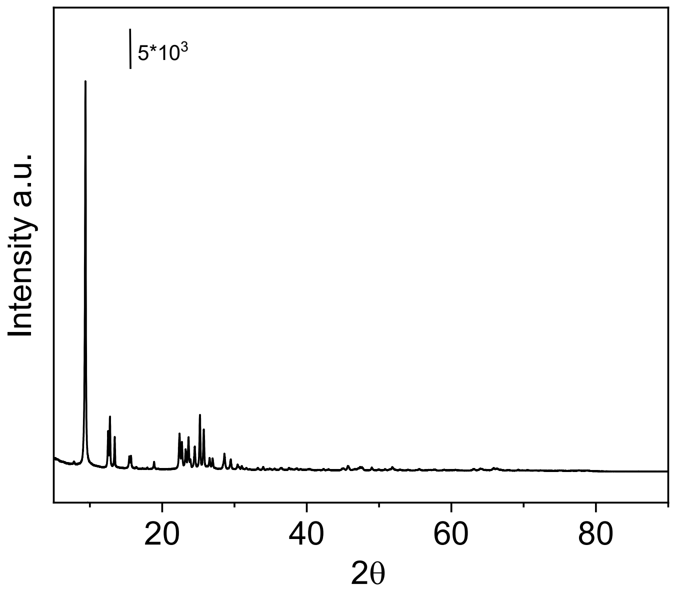

Figure S5. XRD power diffraction pattern of H-FER samples.

Table S2. Structural, chemical composition of parent FER and distribution of framework aluminum.

Sample	Si/Al[1]	S_{BET}	V_{micro}	Co/Al[1]	Al pairs[1]		Al single[1]		Al pairs in β[2]
		m^2/g	cm^3/g		%	mmol/g	%	mmol/g	mmol/g
H-FER	8.6	257	0.12	0.33	66%	1.09	34	0.56	88

[1] From the chemical analysis done by the X-ray fluorescence spectroscopy (ARL 9400 XP, Thermo ARL).

[2] From analysis of UV-Vis spectra of fully exchanged Co-FER[5,6]

The quantitative analysis of Al distribution in ferrierite (FER):

Al pairs stand for two Al atoms able to stabilize Co(II) hexaaqua complex in hydrated zeolite and bare Co(II) cation in the dehydrated zeolite. Thus, their concentration is given by the equation (E1)

$$[Al_{pair}] = 2 \times [\mathrm{Co(II)}] \qquad \text{(E1)}$$

where [Co(II)] is the concentration of Co from chemical analysis, or concentration of bare Co(II) cations from FTIR in the region of antisymmetric T-O-T vibrations of the zeolitic lattice of fully exchanged Co-FER. [5,6]

Single Al atoms represent the fraction of Al atoms not participating in the stabilization of divalent cations or their complexes, and can be calculated based on the dependence (E2).

$$[Al_{single}] = [Al] - 2 \times [Co(II)] = [Al] - [Al_{pair}] \qquad \text{(E2)}$$

where [Al] is total concentration of framework Al atoms from chemical analysis. Exclusive presence of tetrahedrally coordinated Al atom (framework Al atoms) in the FER sample was confirmed by ^{27}Al MAS NMR (available on the request).

The results of Al distribution in ferrierite Si/Al 8.6 (Tosoh Corporation, Japan) was summarised in the Table S2.

The quantitative analysis of the siting of divalent cations in β cationic site in studied FER (which corresponds to the concentration of Al pairs forming β cationic site with planar geometry) was calculated based on the analysis of the UV-Vis spectra of fully exchanged Co-FER.[5,6]

References

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