

Supporting material

Degradation of Trichloroethylene by Catalytic Oxidation over Fe₂O₃-Mayenite

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1 **S1 Experimental details**

2 **Catalyst preparation and characterization**

3 Mayenite was prepared by adding a stoichiometric mixture of 41.5 g of $\text{Ca}(\text{OH})_2$ and 50.7 g of
4 $\text{Al}(\text{OH})_3$ to 1 L of distilled water and grounded to powder under magnetic stirring for 4 h at room
5 temperature. The obtained solid was filtered and dried at 120 °C for 8 hours, crushed into fine
6 powder and finally calcined into a furnace at 1000 °C in air for 4 hours.

7 Mayenite loaded with two different amounts of iron (1.5 and 2.0 %) was synthesized by adding an
8 appropriate amount of mayenite to a solution containing the required amount of $\text{Fe}(\text{acac})_3$ dissolved
9 in 500 mL of high-purity toluene. The solution was stirred for 15 minutes then mayenite was added.
10 The slurry was stirred at room temperature for 48 h. Afterwards, toluene was removed by using a
11 rotary evaporator, and the solid was dried under vacuum at 50 °C for 48 h and calcinated at 1000 °C
12 in air for 4 hours.

13 XRD patterns were obtained on a Bruker D8 Advance automatic diffractometer operating with a
14 nickel-filtered $\text{CuK}\alpha$ radiation. Data were recorded in the 2θ range of 4 – 80° with the resolution of
15 0.02°.

16 The BET surface areas of the catalysts were determined by using a Nova Quantachrome 4200e
17 instrument with nitrogen as probe molecule at liquid nitrogen temperature (–196 °C). Before the
18 measurement, mayenite sample was degassed at 200 °C under vacuum for 12 h. The surface area
19 values were determined by using 11-point BET analysis.

20 Temperature programmed reduction (TPR) experiments were carried out using a TPD-TPR
21 Autochem 2910 analyzer equipped with a thermal conductivity detector. The reduction of the
22 samples (10 – 20 mg) was studied from 25 to 800 °C with a thermal ramp of 10 °C min^{-1} using a
23 $\text{N}_2:\text{H}_2$ flow (10% H_2) of 50 mL min^{-1} .

24 The morphological and elemental analysis of the catalysts were performed by a scanning electron
25 microscope (SEM, Tescan Vega LMU) equipped with a X-Ray energy dispersive microanalysis of

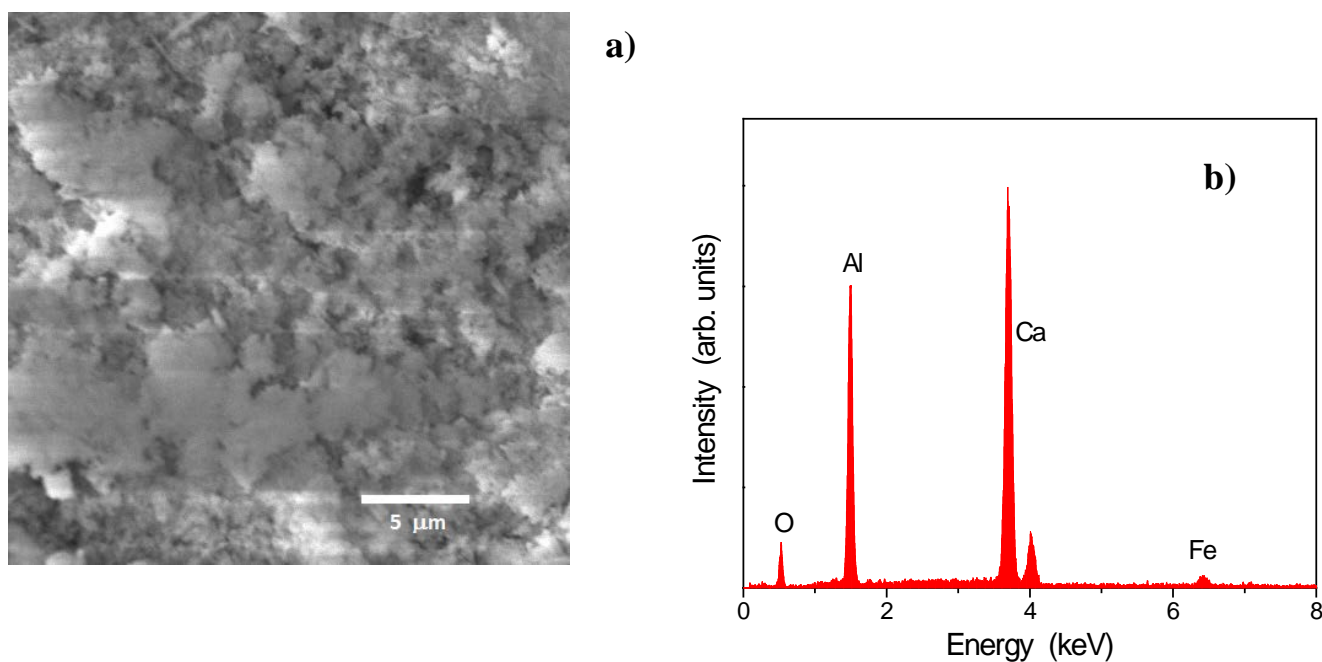
1 elements having an atomic number > 4 , with a resolution of Mn KV less than 123 eV (100.000 cps)
2 (EDX, Bruker Quantax 800). Mayenite samples have been placed on stubs covered by carbon disk.
3 SEM images have been obtained by secondary electrons (SE) with an accelerating voltage of 20.00
4 KV. The EDX spectra were obtained with an accelerating voltage of 20.00 KV and with a WD of
5 15.0 mm. X-Ray intensities were converted in wt% elements by a standardless ZAF quantification.
6 Additionally Fe-mayenite was characterized by field emission scanning electronic microscope
7 (FESEM) using a ZEISS ULTRA 55 equipped with an energy dispersive X-Ray spectroscopy
8 device. This coupled-technique obtains semi-quantitative information of the chemical composition
9 of the samples and information about the distribution of the elements in the material.
10 X-ray photoelectron spectroscopy (XPS) analysis was performed with a SPECS spectrometer
11 equipped with a Phoibos 150MCD-9 multichannel analyzer using non-monochromatic $MgK\alpha$
12 (1253.6 eV) irradiation. Spectra were recorded using analyser pass energy of 30 eV, an X-ray power
13 of 50 W and under an operating pressure of 10^{-9} mbar. Peak intensities have been calculated after
14 nonlinear Shirley-type background subtraction and corrected by the transmission function of the
15 spectrometer. During data processing of the XPS spectra, binding energy (BE) values were
16 referenced to C1s peak (284.5 eV). CasaXPS software has been used for spectra treatment.

17 **S2 Mayenite catalysts characterization**

18 **SEM images and EDX of 2.0% Fe/Mayenite**

19 Figure S1 shows a SEM image and the EDX results of a 2%Fe/mayenite. A porous material,
20 characterized by large pores with dimensions of μm (macropores) and nm (mesopores) is observed.
21 EDX results are reported in Figure S1b, showing that the catalyst is composed of calcium,
22 aluminium, oxygen and iron with an approximate content of 34%, 40%, 26%, and 2 wt.%
23 respectively.

24



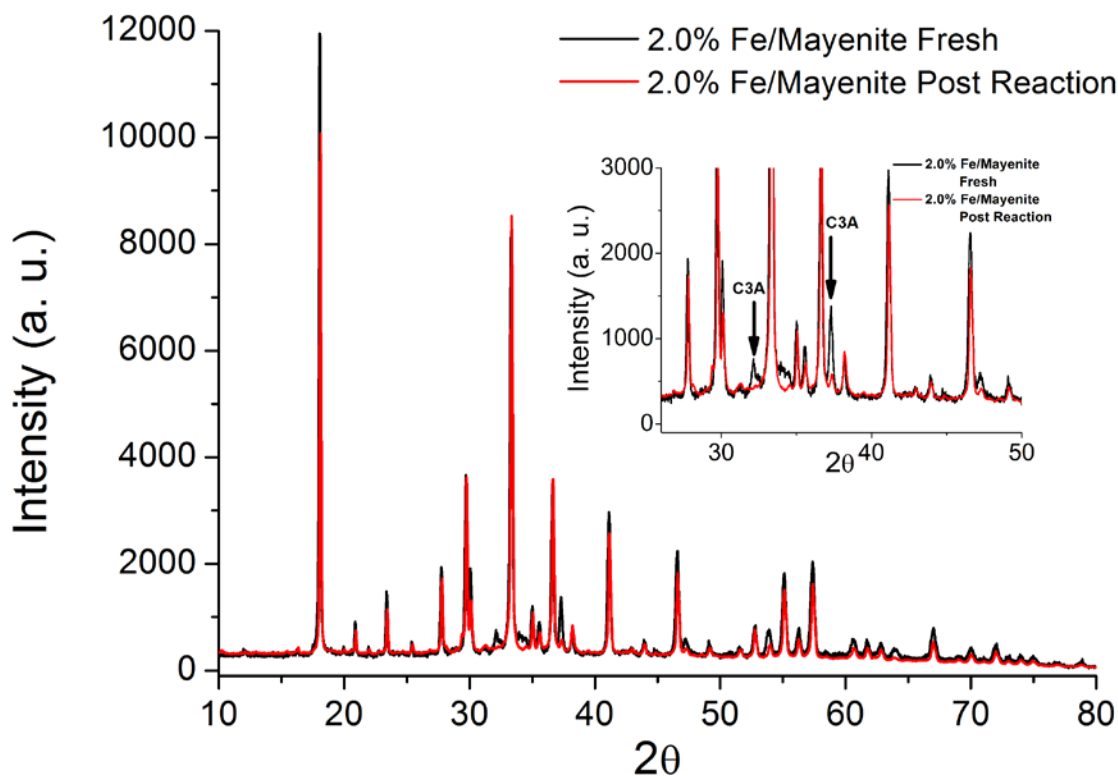
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4 **Figure S1.** a) SEM image of 2.0% Fe-mayenite; b) EDX spectrum of 2.0% Fe-mayenite

5 **S3 Catalyst Stability**

6 **XRD patterns of 2.0% Fe/Mayenite**

7 XRD patterns of 2.0% Fe/Mayenite before (black line) and after (red line) stability test are reported
 8 in Fig. S2. As it can be seen, only minor changes in some peaks are observed, in particular the
 9 disappearance of the peaks at 32.2° and 37.3° attributed to $\text{Ca}_3\text{Al}_2\text{O}_6$ (C3A) (*J. Solid State Chem.*,
 10 177, **2004**, 866-874; *J. Therm. Anal. Calorim.*, 105, **2011**, 427-434) is observed after reaction,
 11 indicating that probably this impurity has evolved to the formation of the mayenite phase during the
 12 reaction (*Appl. Catal. B: Environ.*, 204, **2017**, 167–172). No peaks assigned to CaCO_3 , CaCl_2 or
 13 FeCl_3 were observed in the catalysts.



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2 **Figure S2.** XRD patterns of 2.0% Fe/Mayenite before (black line) and after (red line) stability test.

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The inset shows a detail of the range $25 < 2\theta < 50$

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6 **SEM images and EDX of 2.0% Fe/Mayenite after reaction**

7 Figure S3 shows a SEM image (a) and the relative EDX spectrum (b) of the 2% Fe/mayenite
 8 sample after the stability test. The comparison with the Figure S2, reveals that the 2.0% Fe-
 9 mayenite, maintained the morphology (with mesopores and macropores) even after the 12 hours-
 10 long oxidative reaction with TCE. Nevertheless, the EDX analysis showed the presence of chlorine
 11 on the catalyst (4 wt.%) after reaction,

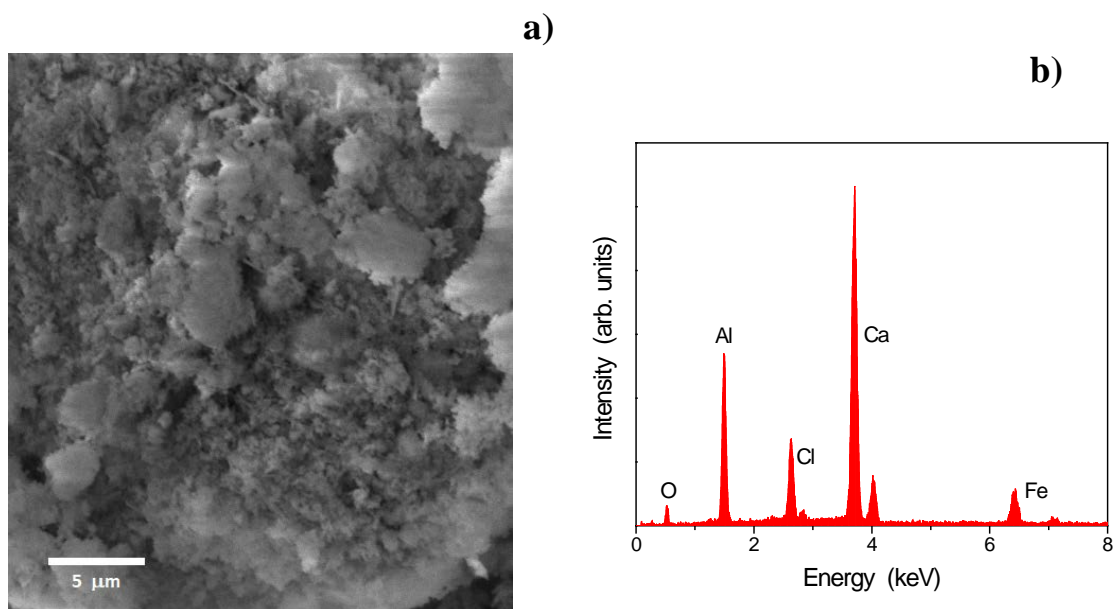


Figure S3. SEM image and relative EDX spectrum of 2% Fe-mayenite after reaction.

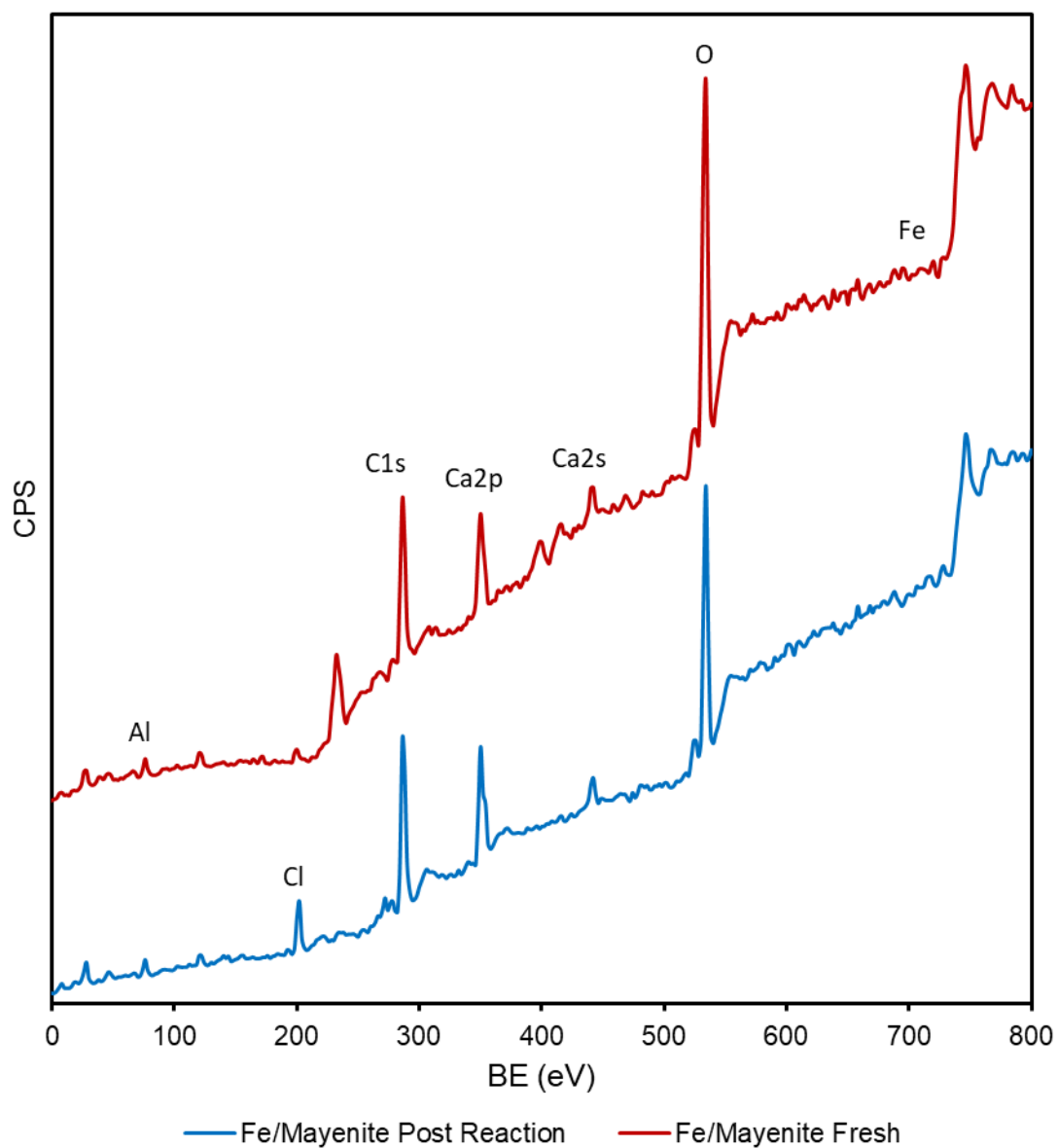
XPS analyses of mayenite catalysts

Fig. S4 shows the XPS spectra of the mayenite containing iron before and after reaction. The wide scan survey spectra of both catalysts (Fig. S4a) showed the appearance of the binding energies of C, Ca, Al, Fe and O. In addition, the binding energy of Cl around 200 eV is also observed in the sample after reaction. The Ca(2p) peaks are located at 347.3 and 350.9 eV and they are ascribed to the Ca(2p_{3/2}) and Ca(2p_{1/2}) core levels of Ca²⁺ ions respectively (*Appl. Surf. Science*, 133, **1998**, 33-46). The peak at 73.8 eV is associated to Al (2p) and is representative of Al³⁺ in the mayenite structure (*Chin. J. Phys.*, 56, **2018**, 252-260). The binding energies of the O (1s) peaks appear at 530.9 eV (*Appl. Surf. Science*, 133, **1998**, 33-46). The peak at 200 eV is only observed in the sample after reaction and it corresponds to the binding energy of Cl (2p) with two contributions at 200 and 189.7 eV characteristic of Cl (2p_{3/2}) and Cl (2p_{1/2}) for ionic chlorine (Cl⁻) (*Chem Pap.*, 71, **2017**, 712545-2555). It must be pointed out, that the presence of this peak in the sample after reaction is coincident with a decrease in the relative intensity of the O peak at 530.9 eV indicating a decrease of the oxygen surface species during the reaction. The broad and low intense peak around 710-712 eV is associated to Fe (2p) levels. As it can be seen in Fig. 7 of the main text, the sample

1 before reaction shows a complex multiplet-split Fe 2p XPS spectra and at least two contributions
2 are observed, the first one is centred at 709.5 eV and the second one, that is more intense, is centred
3 at 711.8 eV. These peaks have been assigned to the Fe²⁺ (2p_{3/2}) and Fe³⁺ (2p_{3/2}) respectively,
4 indicating the formation of Fe₂O₃ probably together with Fe₃O₄ (*Chem Pap.*, 71, **2017**, 712545-
5 2555; *Surf. Interface Anal.*, 36, **2004**, 1564-1574). After reaction, an increase in the band centred at
6 711.8 eV together with a small shift to highest eV is observed. This is indicating some changes in
7 the iron species that could be related with the disappearance of the Fe²⁺ contribution in the Fe₃O₄
8 phase or with the formation of FeCl₃ (*Surf. Interface Anal.*, 36, **2004**, 1564-1574). Nevertheless the
9 content of iron is too low to clearly identify the changes produced in the iron species.

10 It is clear from the XPS study that after 12 hours of reaction some chloride species are formed but
11 the oxygen content in the catalyst surface is still very high. This indicates that the formation of Cl⁻
12 during the reaction does not result in an irreversible adsorption of the Cl⁻ on the ionic vacancies as it
13 occurs with pure mayenite (*Sci. Rep.* **2019**, 9, 425.).

XPS survey spectra



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Figure S4. XPS survey spectra of the Fe/mayenite (2% Fe) before and after reaction