

Supporting information

On the reaction mechanism of MnO_x/SAPO-34 bifunctional catalysts for the conversion of syngas to light olefins

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Materials

Manganese oxide (labelled MnO_x) was prepared by thermal decomposition of MnCO₃ (Sigma-Aldrich, 377449, ≥99.9 %) under 100 NmL.min⁻¹ of 25% H₂-N₂ flow at 410 °C (heating rate 5 °C.min⁻¹) for 12 h. After cooling down to room temperature, the sample was slowly passivated in ambient air to avoid pyrophoric effect.

SAPO-34 zeotype was synthesized mixing 84 g of Al isopropoxide (Sigma Aldrich, 220418, ≥98%) and 170 mL of TEOAH (Sigma Aldrich, 86633, 40% in H₂O, 3% K) under stirring (750 rpm) at RT for 1h30 before pouring 3.7 g of SiO₂ (Evonik, Aerosil® 200, >99%) and maintaining the mixture under stirring at RT for 1 h. Finally, 47 g of H₃PO₄ (Honeywell, 30417, 85 wt%) and 68 g of deionized water were added. After 3 h of additional stirring, the overall mixture was firstly hydrothermally treated at 100 °C for 12 h and in a second step, treated at 200 °C for 48 h (autogenous pressure, no stirring in both cases). After filtration, the solid was dried at 100 °C for 24 h, calcined at 200 °C (heating rate 1 °C.min⁻¹) for 2 h and finally at 550 °C (heating rate 0.5 °C.min⁻¹) for under 80 NmL.min⁻¹ of air flow.

Catalytic measurements

Catalytic performances of MnO_x, MnO_x-SAPO-34 Separated layered (SLB), layered (LB) and multi-layer (ML x3 and ML x4) catalytic beds were compared in a continuous fixed-bed stainless steel reactor (L = 400 mm, \varnothing_{int} = 6.35 mm). In case of LB, MnO_x (0.600 g, 100–160 μm) and SAPO-34 (0.300 g, 100–160 μm) were placed between 2 portions of SiC (1.238 g, 125 μm for each) leading to a height of 8 cm. For SLB, MnO_x and SAPO-34 were separated with a layer of SiC (0.825 g) equivalent to the two other ones leading also to a height of 8 cm. For the ML x3, the two layers of MnO_x and the layer of SAPO-34 were equivalent (0.300 g each) to have 0.900 g of catalyst. For the ML x4, the two layers of MnO_x were the same as ML x3 (0.300g each) and the 2 layers of SAPO-34 were equivalent, with 0.150 g each. The different arrangements used in this study are illustrated in Table. S1.

Before reaction, the catalyst was pre-treated *in situ* at 410 °C for 30 min (heating rate of 5 °C.min⁻¹) under a flow of pure H₂ (30 NmL.min⁻¹) at atmospheric pressure. Then, the reactor was purged with argon and the pressure was increased to 25 bar. The reactor was then flushed with the reactant gas mixture (H₂/CO/Ar:64/26/10, 78 NmL.min⁻¹) at 410 °C. The outlet flow was decompressed and periodically injected in an Agilent 7890A gas chromatograph (GC) connected online. All the lines connecting the reactor with the GC were kept at 200 °C to avoid product condensation. The GC was equipped with three channels: the first one consisted of two series connected of HP PLOT 5A molecular sieve column (for H₂ and CO) and a HP PLOT Q

molecular sieve column (for CO₂ and H₂O) connected to a TCD detector, while the second channel consisted of a HP INNOWAX capillary column (for methanol) connected to a FID detector and finally the third channel consisted of a GS-Q capillary column (for hydrocarbons) connected to another FID detector.

Table. S1: Labelling, illustration and number of layer of the different catalytic bed arrangements.

Labelling	Arrangement	Number of layer	Number of contact
MnO _x		1	-
SAPO-34		1	-
SDL		2	0
DL		2	1
MLx3		3	2
MLx4		4	3

Mechanical mixtures were prepared mixing vigorously different amounts of MnO_x and SAPO-34 powders sieved at 105-180 μm. Catalytic testing was achieved using a fixed-bed reactor (L = 135 mm, ϕ_{int} = 6.35 mm) in which a thermocouple was inserted. Before reaction, the catalyst was pre-treated *in situ* at 430 °C for 4 h (heating rate of 10 °C.min⁻¹) under a flow of pure H₂ (20 NmL.min⁻¹) at atmospheric pressure. Then, the reactor was purged with N₂ and the pressure was increased to 25 bar. The reactor was then flushed with the reactant gas mixture (H₂/CO/Ar:60/30/10, 26.0 NmL.min⁻¹) at 410 °C. The molar concentrations of CO, H₂, CH₄, C2-C4 olefins and paraffins were measured online using a microGC (Fusion/ChemLys, molecular sieve and alumina Na₂SO₄ columns, TCD detector) while CO₂ was analyzed with another microGC (3000/Inficon, Plot-U column, TCD detector).

Characterization methods

Powder X-ray diffraction patterns were recorded between 4 and 80° (step of 0.02°, 0.5 s of counting per point) using a Bruker D8 Advance A25 diffractometer equipped with a Ni filter (Cu K_α radiation: 0.154184 nm) and a one-dimensional multistrip detector (Lynxeye, 192 channels on 2.95°). Samples were previously crushed and sieved below 50 μm to avoid preferential orientations. The Powder Diffraction File (PDF) database of the International Center for Diffraction Data (ICDD) was used for indexation. The crystallite size was determined measuring the width at half maximum of bands with the I-width method and using the Debye-Scherrer equation.

MicroRaman spectra was recorded with a LabRAM HR spectrometer (Horiba) using the exciting line at 514.53 nm of an Ar⁺ ion laser, X50 objective and CCD open electrode detector cooled down to -75 °C. The spectral resolution was 4 cm⁻¹. The laser power at the samples was limited to 100 μW so that the laser heating was negligible. *In situ* measurements were performed in a THMS600 cell coupled with a TMS94 programmer (Linkam). The temperature gradient between the heating sole and the upper part of the powder sample was previously determined and corrected.

A SAPO-34 sample was dissolved into H₂SO₄+HNO₃+HF at boiling point before using an ICP-OES Activa (Horiba) spectrometer to perform the analyses for Al and P. For the Si determination, the solid was fused with lithium tetraborate into a Pt-Au crucible at 1100 °C. The obtained solid was then dissolved into HCl 20 wt% before using an ICP-OES Activa (Horiba) spectrometer to perform the analyses.

The BET Specific Surface Areas (S_{BET}) were measured by nitrogen physisorption at -196 °C using a Micromeritics ASAP 2020 instrument and applying the BET method. The samples were previously outgassed under vacuum of 0.1 Pa for 2 h at 400 °C.

In situ DRIFT spectra were achieved with a Nicolet 6700 FTIR spectrometer (Thermo Scientific) equipped with Praying Mantis™ High Temperature Reaction Chamber (Harrick, model HVC-DRP-4) and MCT detector cooled by liquid N₂. The spectral resolution was 4 cm⁻¹. The temperature gradient between the regulation thermocouple and the upper part of the powder sample was previously determined and corrected.

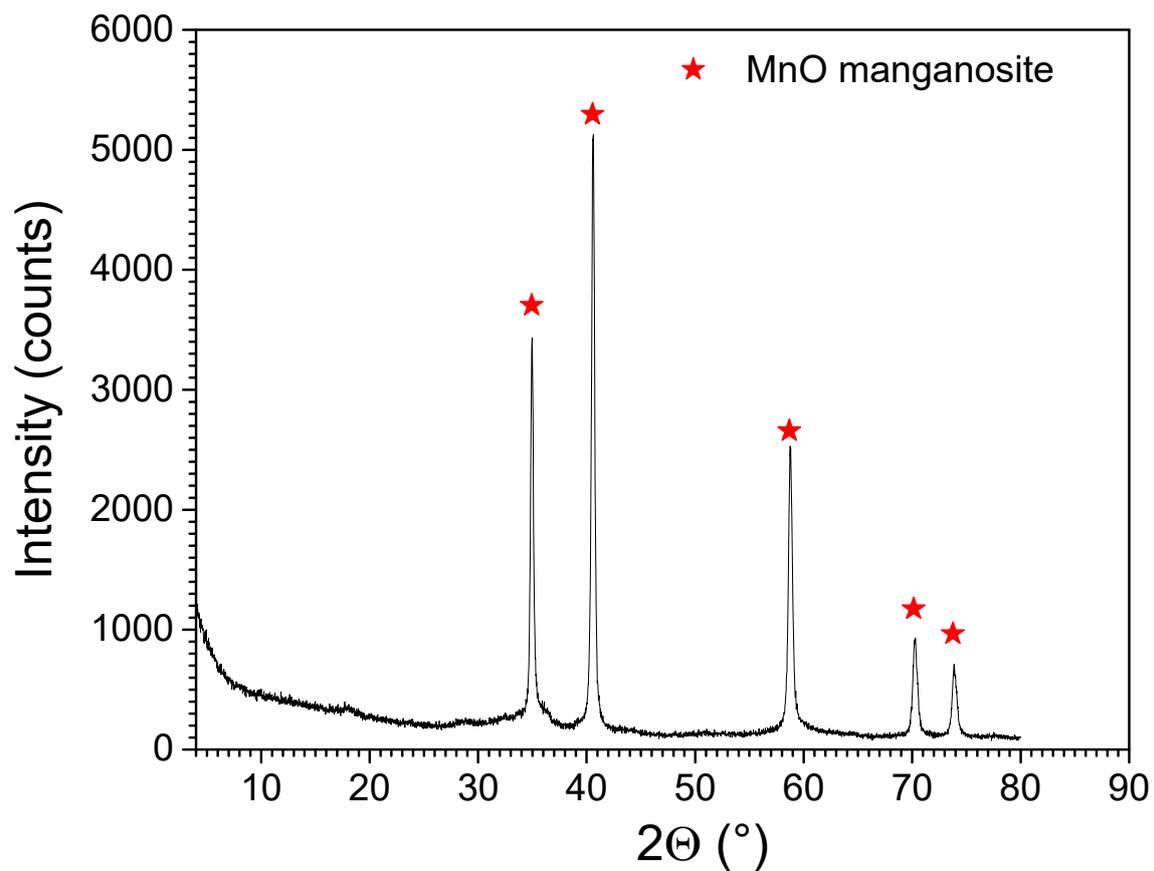


Fig. S1: XRD diagram of as-prepared MnO_x sample. The diffraction peaks were indexed with the PDF 75-1090 pattern corresponding to the MnO manganosite phase.

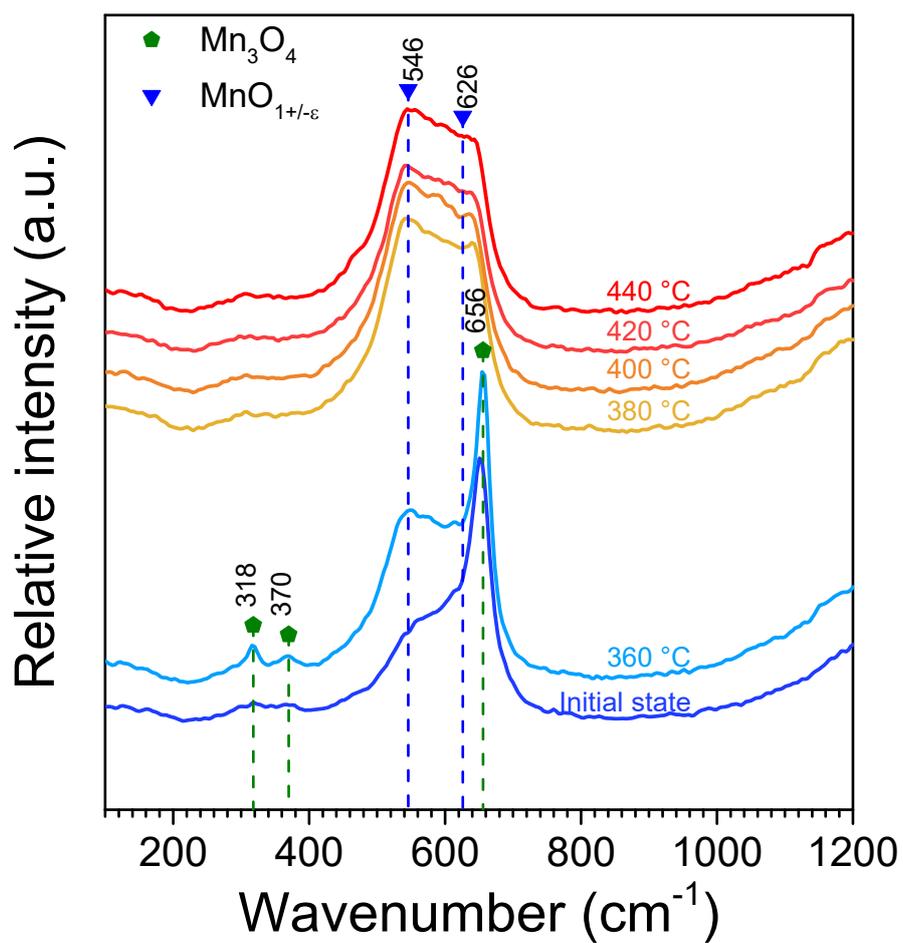


Fig. S2: *In situ* Raman spectra recorded at RT of MnO_x sample at the initial state and after treatment for 15 min under 50 NmL.min⁻¹ of 10%H₂-N₂ flow at different temperatures.

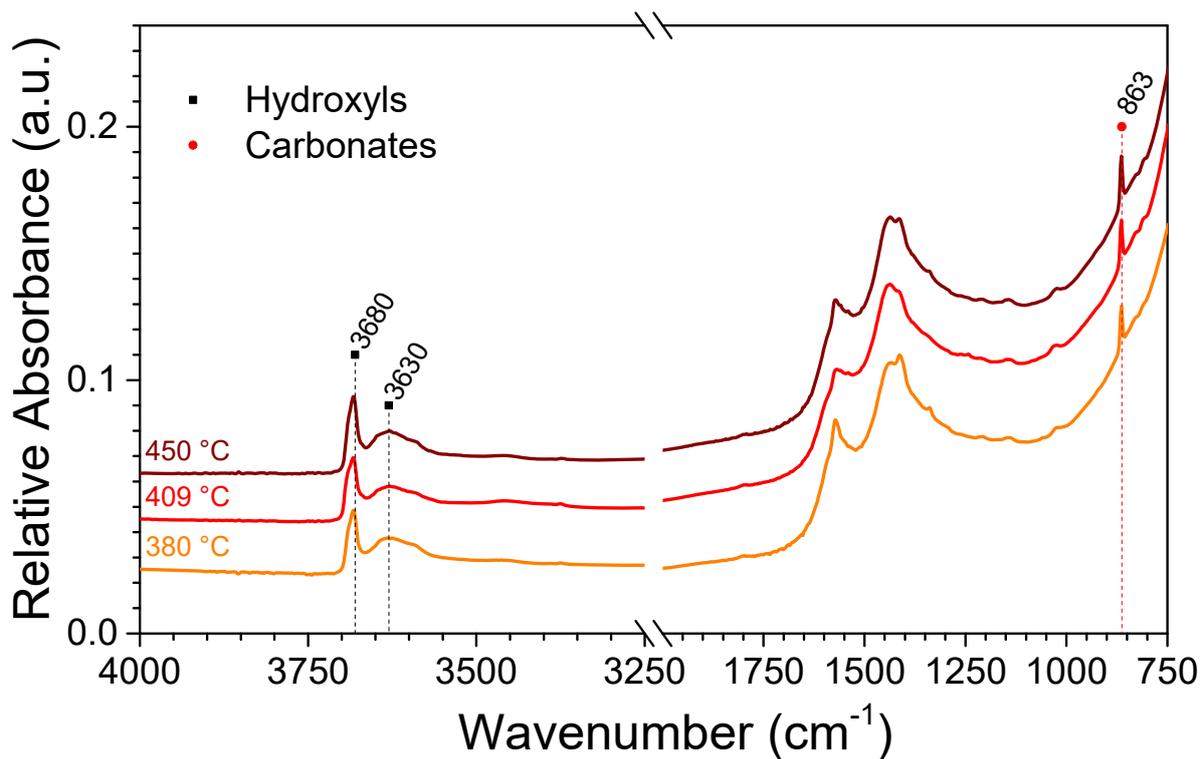


Fig. S3: *In situ* DRIFT spectra of MnO_x recorded under 20 NmL.min⁻¹ of H₂ flow at different temperatures. The backgrounds corresponded to the spectra of dehydrated KBr powder recorded at the same temperatures.

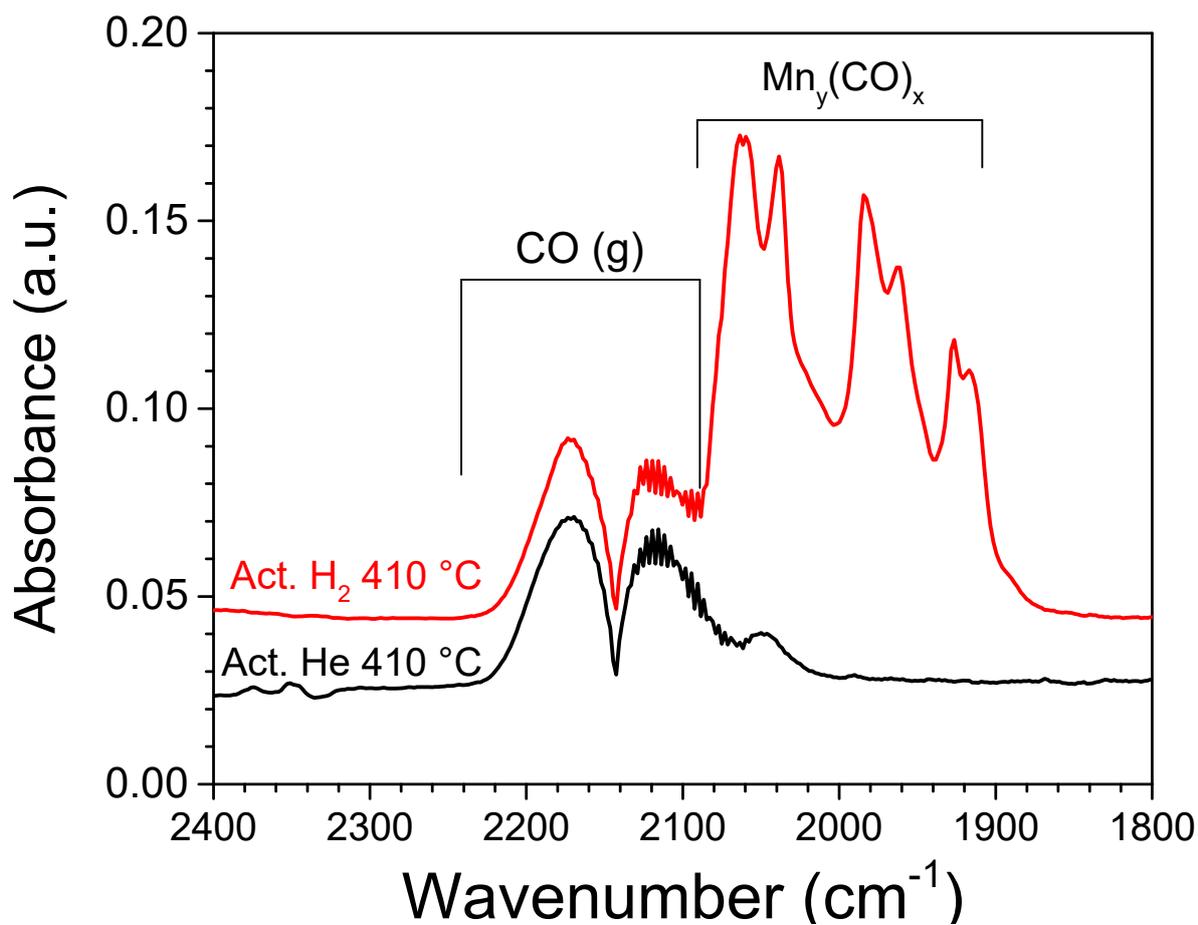


Fig. S4: *In situ* DRIFT spectra of MnO_x sample recorded at -2 °C under 20 NmL.min⁻¹ of 2.5%CO-He flow. The backgrounds corresponded to the spectra recorded under 20 NmL.min⁻¹ of He flow at -2 °C after activation at 410 °C under 20 NmL.min⁻¹ He or H₂ flow for 30 min.

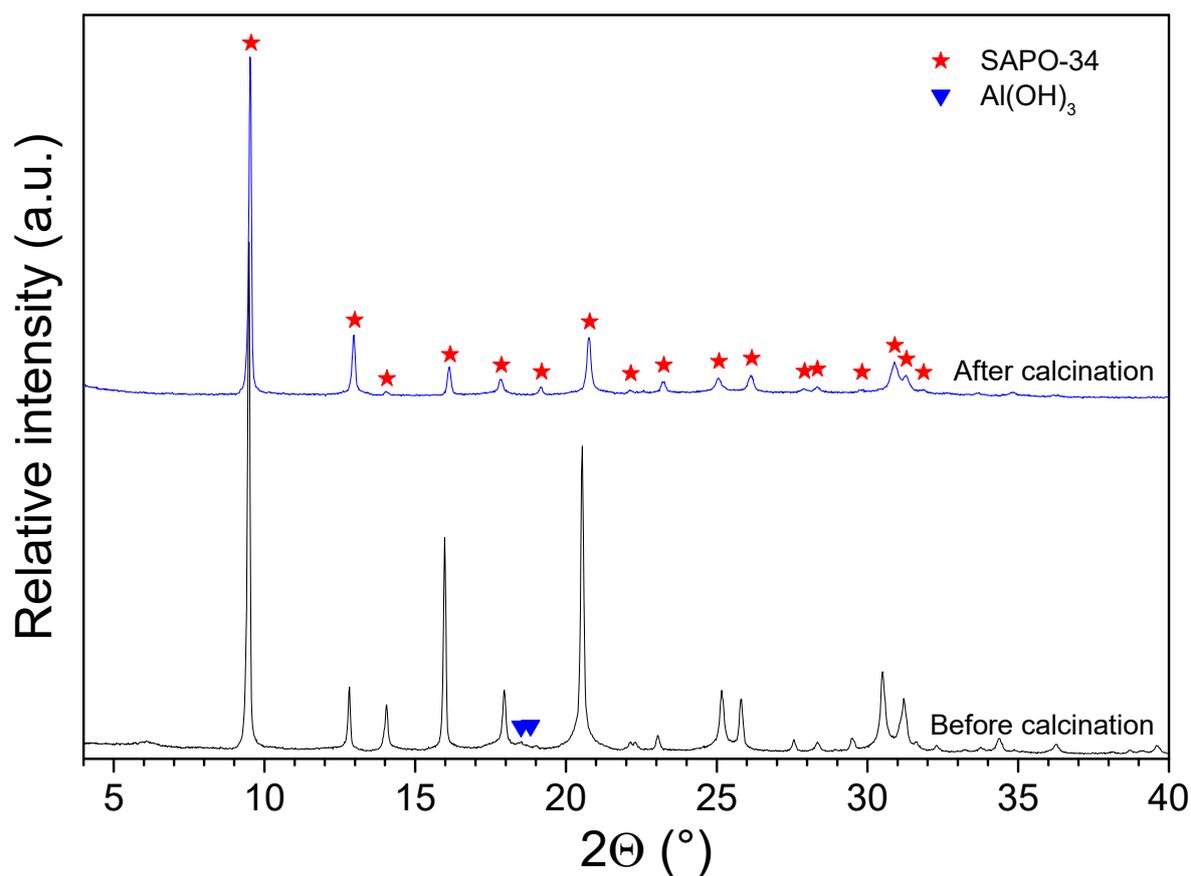


Fig. S5: XRD diagrams of the SAPO-34 powder before and after calcination. The diffraction peaks were indexed with the PDF 47-0429 pattern corresponding to crystalline SAPO-34 with composition Si/Al/P:0.22/1/0.75. Note that traces of $\text{Al}(\text{OH})_3$ (PDF 85-1049 pattern) were detected before calcination suggesting the presence of amorphous Al_2O_3 after calcination. The slight shift and change of relative intensity of peaks are due to the removal of organic species during calcination leading to slight modification of the crystalline structure.^{S1}

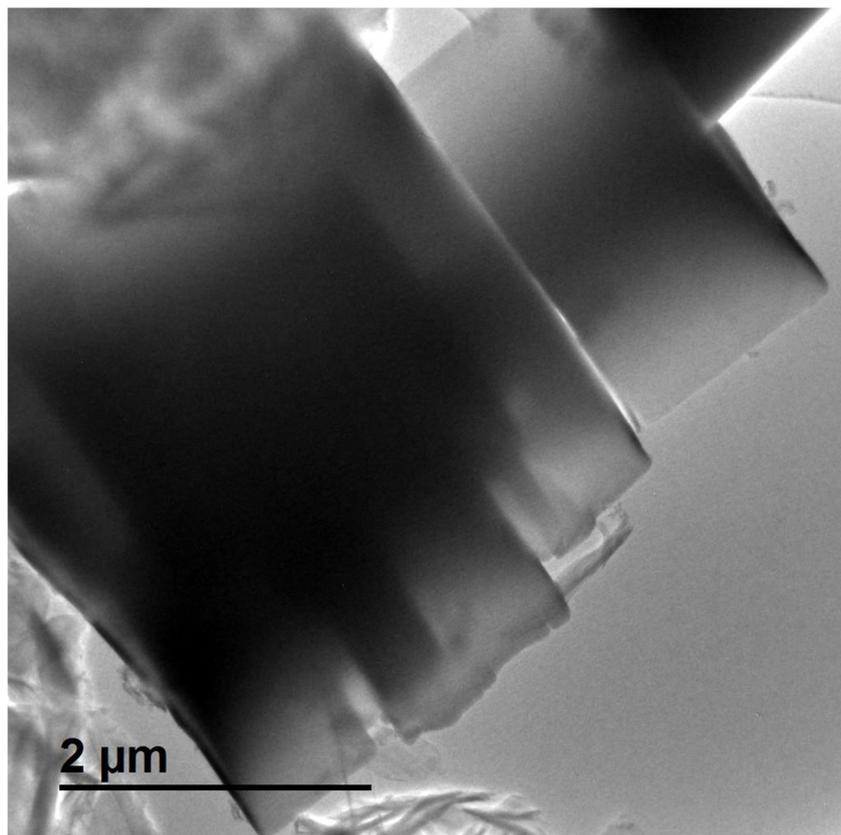


Fig. S6: SEM image of the SAPO-34 powder after calcination.

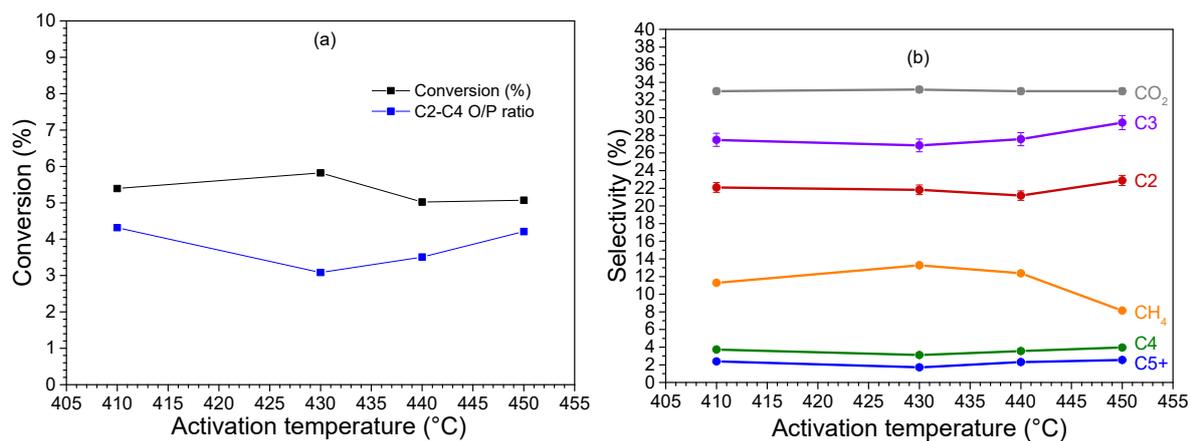


Fig. S7: (a) evolution with the activation temperature of (a) the conversion and the C2-C4 O/P ratio and (b) the selectivity values. Reaction conditions: $m(\text{MnOx})=200$ mg, $m(\text{SAPO-34})=100$ mg, $P=25$ bar, $T=410$ °C, $\text{H}_2/\text{CO}/\text{Ar}=60/30/10$, $\text{WHSV } 87 \text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$.

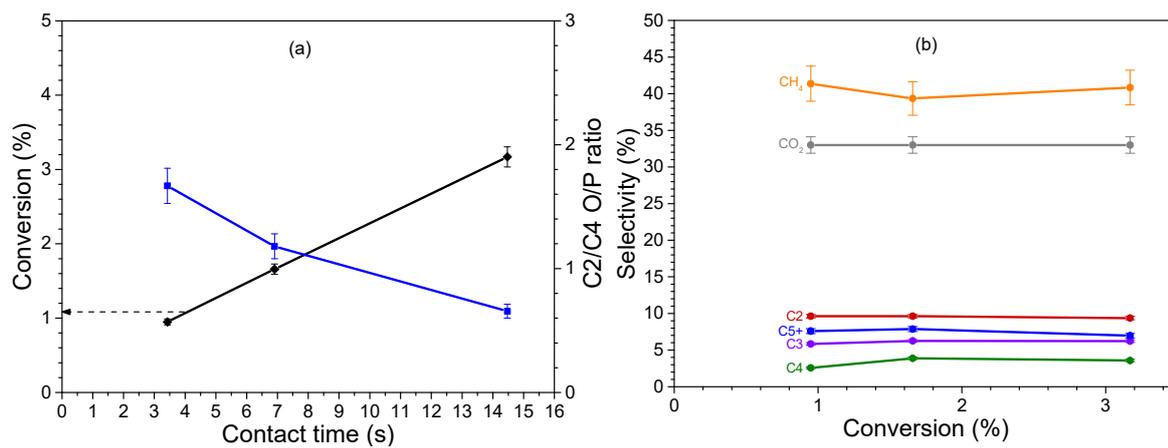


Fig. S8: (a) evolution with the contact time of the conversion and C2-C4 O/P molar ratio and (b) conversion-selectivity curves for MnOx. Reaction conditions: $m(\text{MnOx})=300$ mg, $P=25$ bar, $T=410$ °C, $\text{H}_2/\text{CO}/\text{Ar}=60/30/10$.

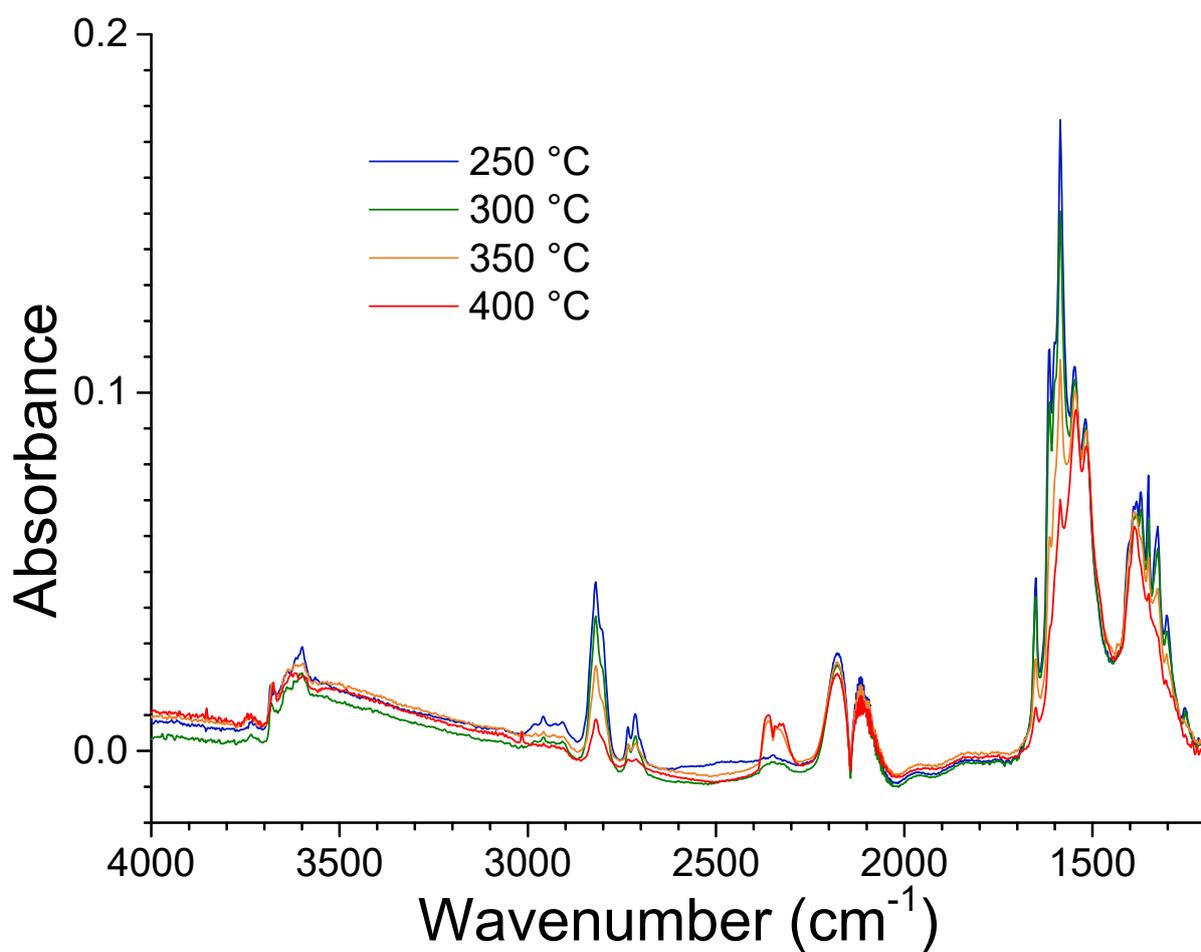


Fig. S9: *In situ* DRIFT spectra of 75%MnO_x-25%SAPO-34 sample recorded at various temperatures under 20 NmL.min⁻¹ of 2.5%CO/7.5%H₂/90%He flow. The backgrounds corresponded to the spectra recorded under 20 NmL.min⁻¹ of He flow after activation at 430 °C under 20 NmL.min⁻¹ H₂ flow for 30 min.

References

S1 R. Vomscheid, M. Briend, M. J. Peltre, P. Massiani, P. P. Man, D. Barhomeuf, *J. Chem. Soc., Chem. Commun.*, 1993, 544–546.