8th International Conference on

Sustainable Solid Waste Management

Catalytic abatement of volatile organic compounds and carbon soot over manganese oxide catalysts

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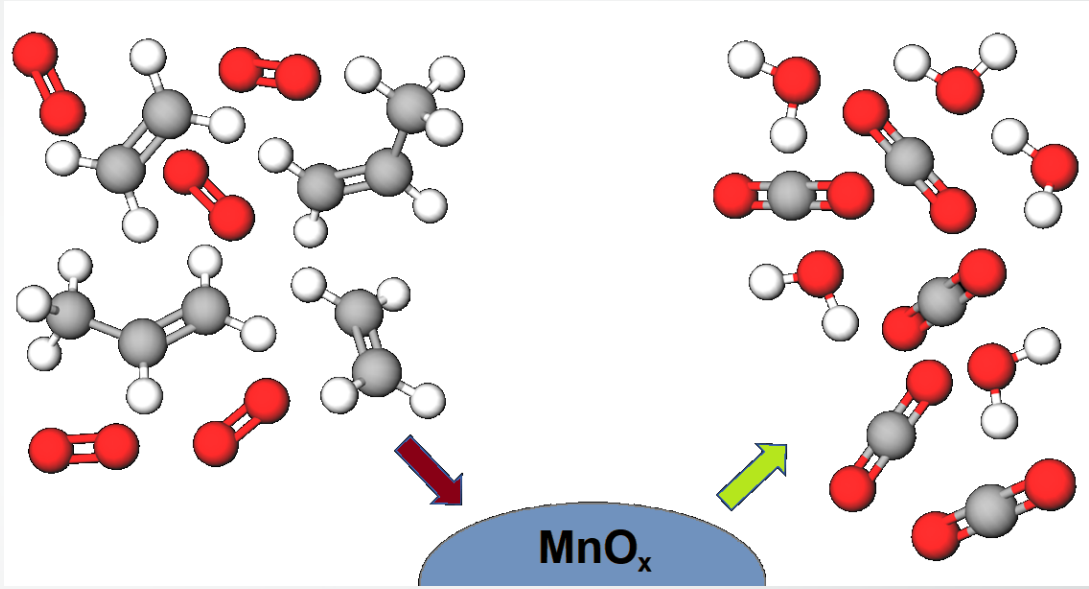
Summary

1. Synthesis procedures

2. Physico-chemical characterization of powder catalysts:

- X-ray powder diffraction
- Specific surface area
- Field-emission scanning electron microscope
- H_2-TPR and soot-TPR
- X-ray photoelectron spectroscopy



Scheme 1. Representation of the catalytic oxidation of VOCs toward CO_2 and H_2O

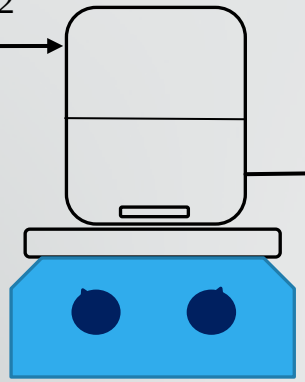
3. Catalytic abatement tests

- VOCs: ethene and propene
- Carbonaceous matter

a) Solution combustion synthesis

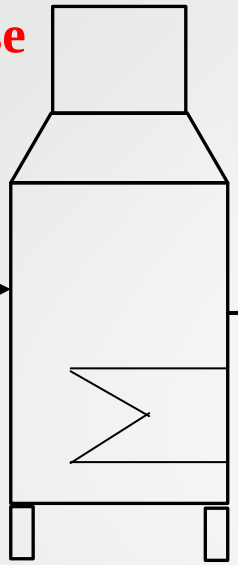
1st Phase

$Mn(NO_3)_2$
$C_6H_8O_7$
H_2O



Homogeneous mix

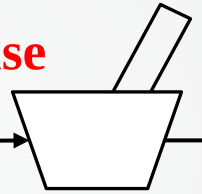
2nd Phase



Raw powders: MnO_x

Temperature ramp: 5-10 °C min^{-1}
Calcination temperature: 600-650 °C
Calcination time: 30 min

3rd Phase



Grinding with mortar and pestle

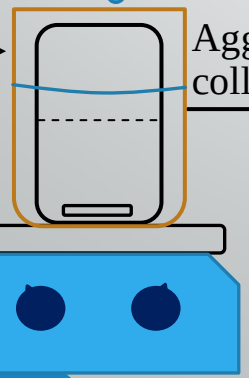
Catalytic powders: MnO_x

b) Sol-gel synthesis

1st Phase

NH_4OH

$Mn(NO_3)_2$
$C_6H_8O_7$
H_2O



Hot bath 60 °C

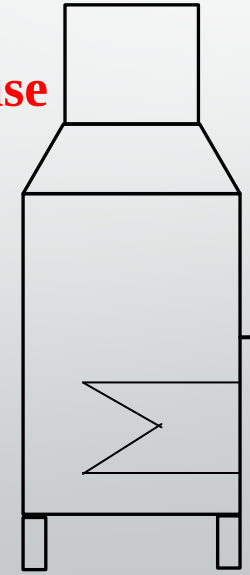
Aggregated colloidal gel

2nd Phase

Rinsing with H_2O

Drying overnight

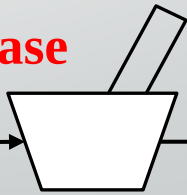
3rd Phase



Raw powders: MnO_x

Temperature ramp: 5 °C min^{-1}
Calcination temperature: 550-650 °C
Calcination time: 2 h

4th Phase



Grinding with mortar and pestle

Catalytic powders: MnO_x

Synthesized catalysts

Solution Combustion Synthesis (SCS):

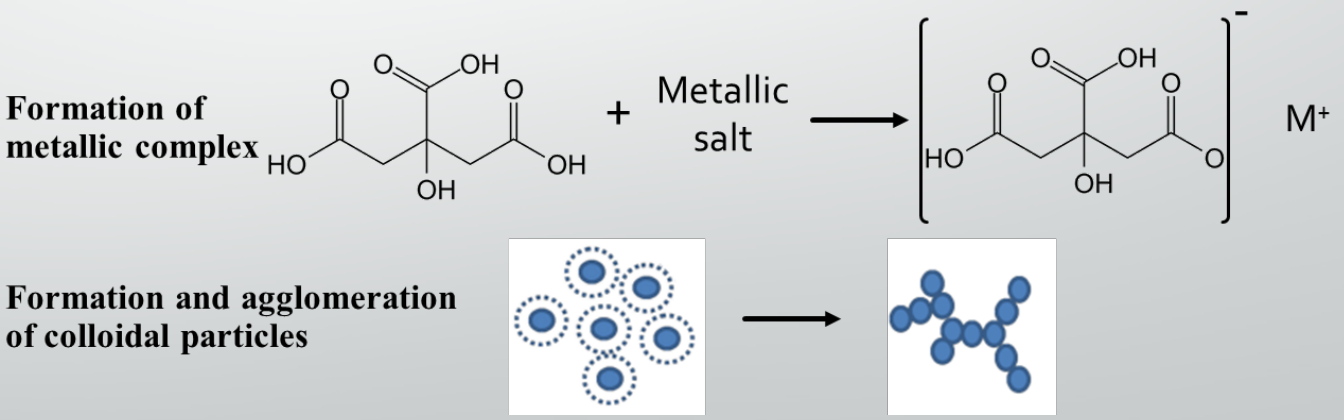
- Mn_2O_3 – SCS
- Mn_3O_4/Mn_2O_3 – SCS

Figure 1. Solution combustion synthesis representative image. Extracted from [1]

$$2\,Mn(NO_3)_2 + \frac{11}{9}\,C_6H_8O_7 + O_2 \rightarrow Mn_2O_3 + \frac{66}{9}\,CO_2 + 2\,N_2 + \frac{44}{9}\,H_2O$$

Sol-gel (SG) synthesis:

- Mn_2O_3 – SG550
- Mn_2O_3 – SG650



Scheme 1. Sol-gel synthesis representative scheme

[1] A. Varma, A.S. Mukasyan, A.S. Rogachev, K. V Manukyan, Solution Combustion Synthesis of Nanoscale Materials, (2016). https://doi.org/10.1021/acs.chemrev.6b00279

Textural properties of the prepared catalysts

Table 1. Textural properties of the fresh powder catalysts.

Catalyst	S_{BET}[a] ($m^2\ g^{-1}$)	V_P[b] ($cm^3\ g^{-1}$)	Crystallites size[c] (nm)
Mn_2O_3-SG550	15	0.12	67
Mn_2O_3-SG650	11	0.10	61
Mn_2O_3-SCS	22	0.15	52
Mn_3O_4/Mn_2O_3-SCS	21	0.13	37 / 53

[a]**S_{BET}:** Specific surface area (BET method)

[b]**V_P:** total volume of pores (BJH method)

[c]**CS:** calculated using Scherrer's formula

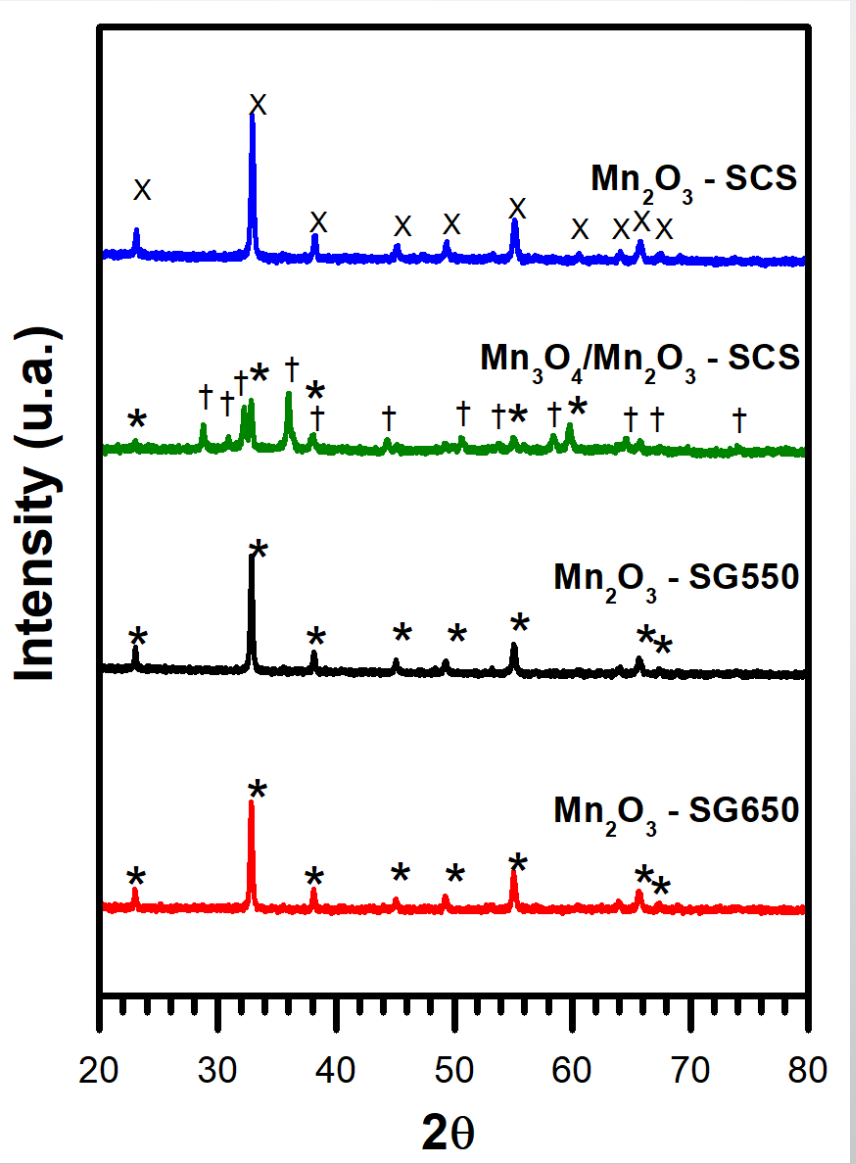
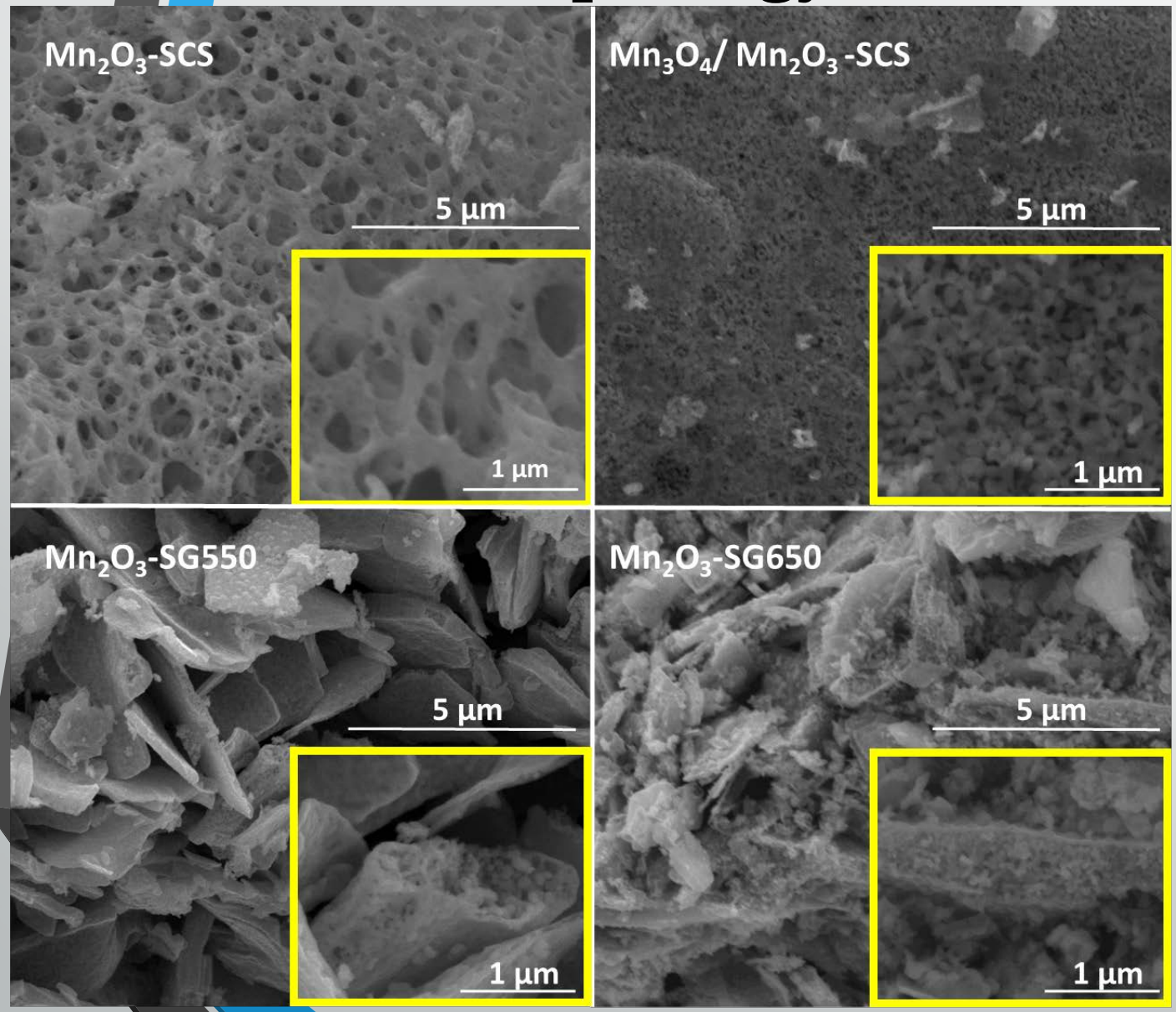


Figure 2. XRD patterns of the synthesized catalysts. Assignments: X= Mn_2O_3 reference code: 01-073-1826; * = Mn_2O_3 reference code: 01-078-0390; † = Mn_3O_4 reference code: 00-024-0734.

Morphology and textural properties



The Solution Combustion Synthesis allowed the preparation of porous sponge-like structures

The powders resulting from the Sol-gel technique consisted in porous nanoplates

Figure 3. FESEM micrographs of the fresh prepared catalysts and the corresponding magnifications.

Temperature-programmed reduction analyses

H_2-TPR PROCEDURE

- **Instrument: TPDRO 1100 ThermoQuest**
- **Mass of catalyst: 20 mg.**
- **Pretreatment: under He:**
  - **Flow rate: 40 mL min^{-1}**
  - **550 °C**
  - **1 h**
- **Analysis: using H_2 5 vol.% in Ar:**
  - **Flow rate: 20 mL min^{-1}**
  - **Temperature range: 50-800 °C**
  - **Temperature ramp: 5 °C min^{-1}**

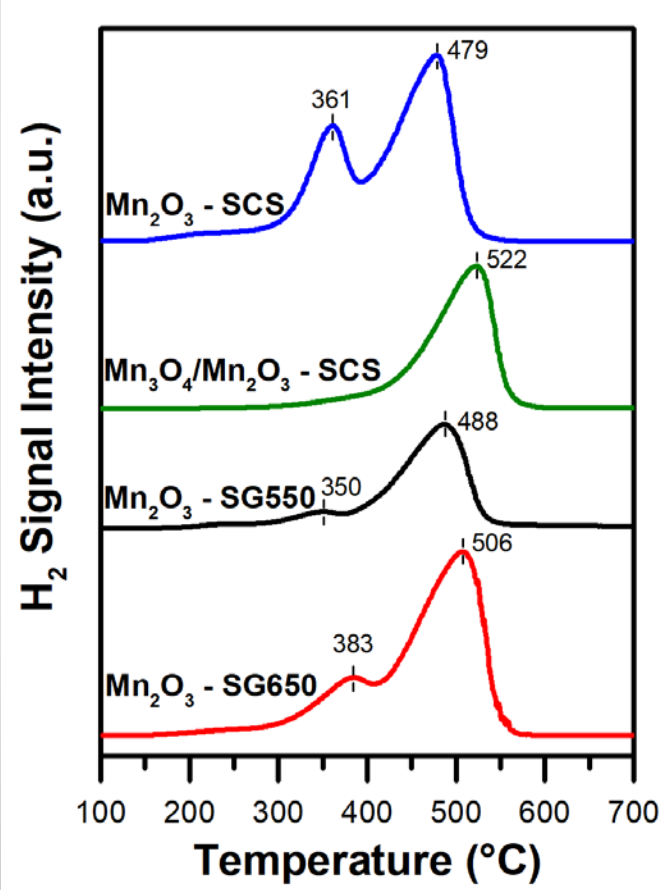


Figure 4. H_2-TPR profiles of the synthesized manganese oxides.

Soot-TPR PROCEDURE

- **Instrument: Quartz U-tube reactor (ID = 4 mm), equipped with CO/CO_2 NDIR analyzer**
- **Fixed-bed content: 45 mg catalyst.**
  150 mg SiO_2
  5 mg soot
- **Pretreatment under N_2:**
  - **Flow rate: 100 mL min^{-1}**
  - **100 °C**
  - **30 min**
- **Analysis: using N_2:**
  - **Flow rate: 100 mL min^{-1}**
  - **Temperature range: 100-700 °C**
  - **Temperature ramp: 5 °C min^{-1}**

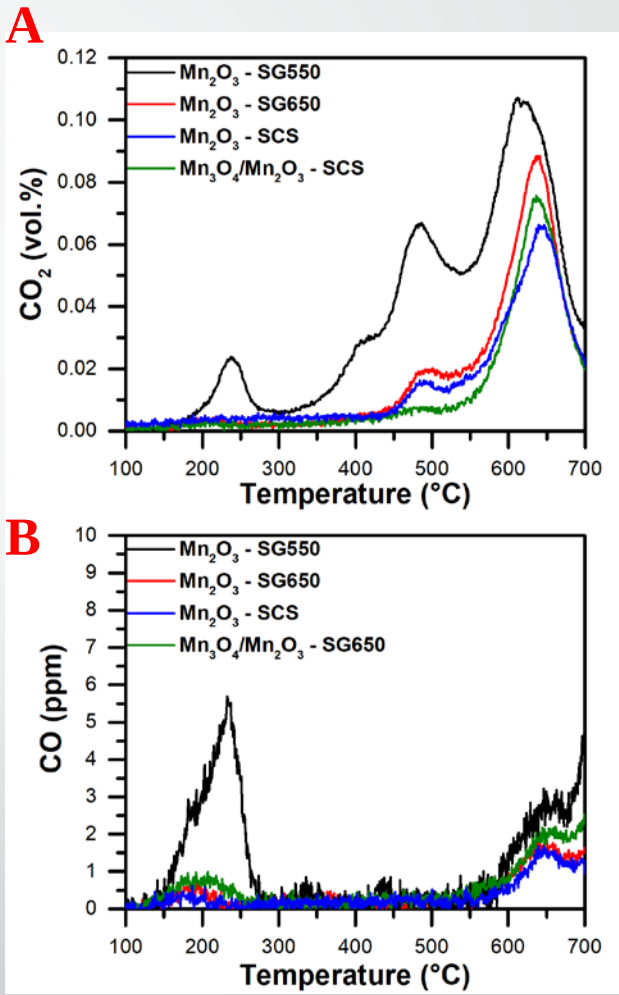


Figure 5. Outlet concentration of CO2 (section A) and CO (section B) observed during the soot-TPR analyses.

X-ray photoelectron spectroscopy (XPS)

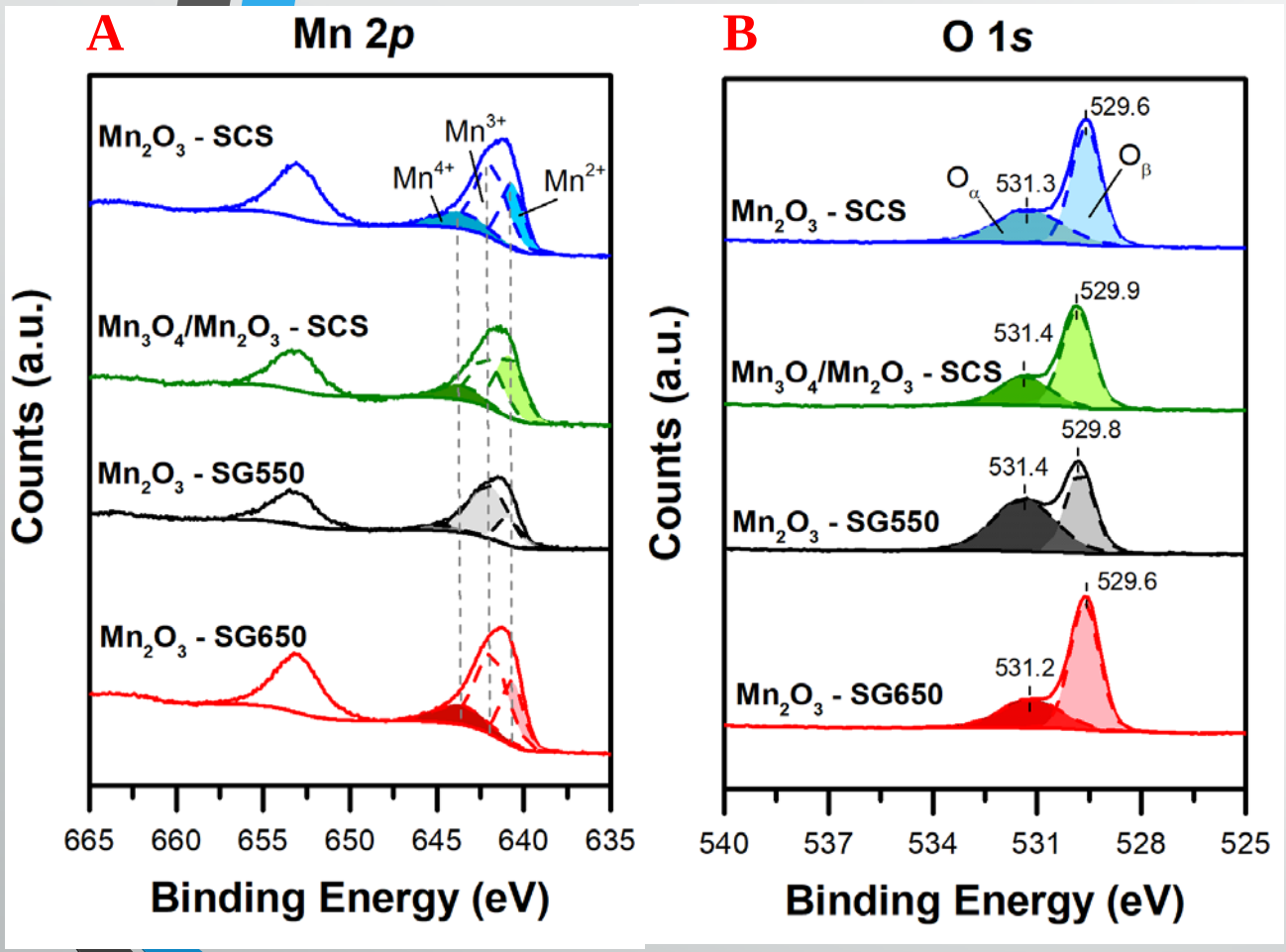


Figure 6. XPS spectra in the Mn 2*p* (section A) and O 1*s* core level (section B)

Table 2. Relative percentages (at.%) of oxygen species calculated from the deconvolution of the O 1*s* XPS spectra.

Catalyst	O_α , OH^- BE (eV)	O_α (at.%)	O_β BE (eV)	O_β (at.%)	O_α/O_β
Mn_2O_3-SG550	531.4	56.7	529.8	43.3	1.31
Mn_2O_3-SG650	531.2	31.8	529.6	68.2	0.47
Mn_2O_3-SCS	531.3	38.5	529.6	61.5	0.63
Mn_3O_4/Mn_2O_3-SCS	531.4	31.8	529.9	68.2	0.47

Catalytic Tests: VOC abatement

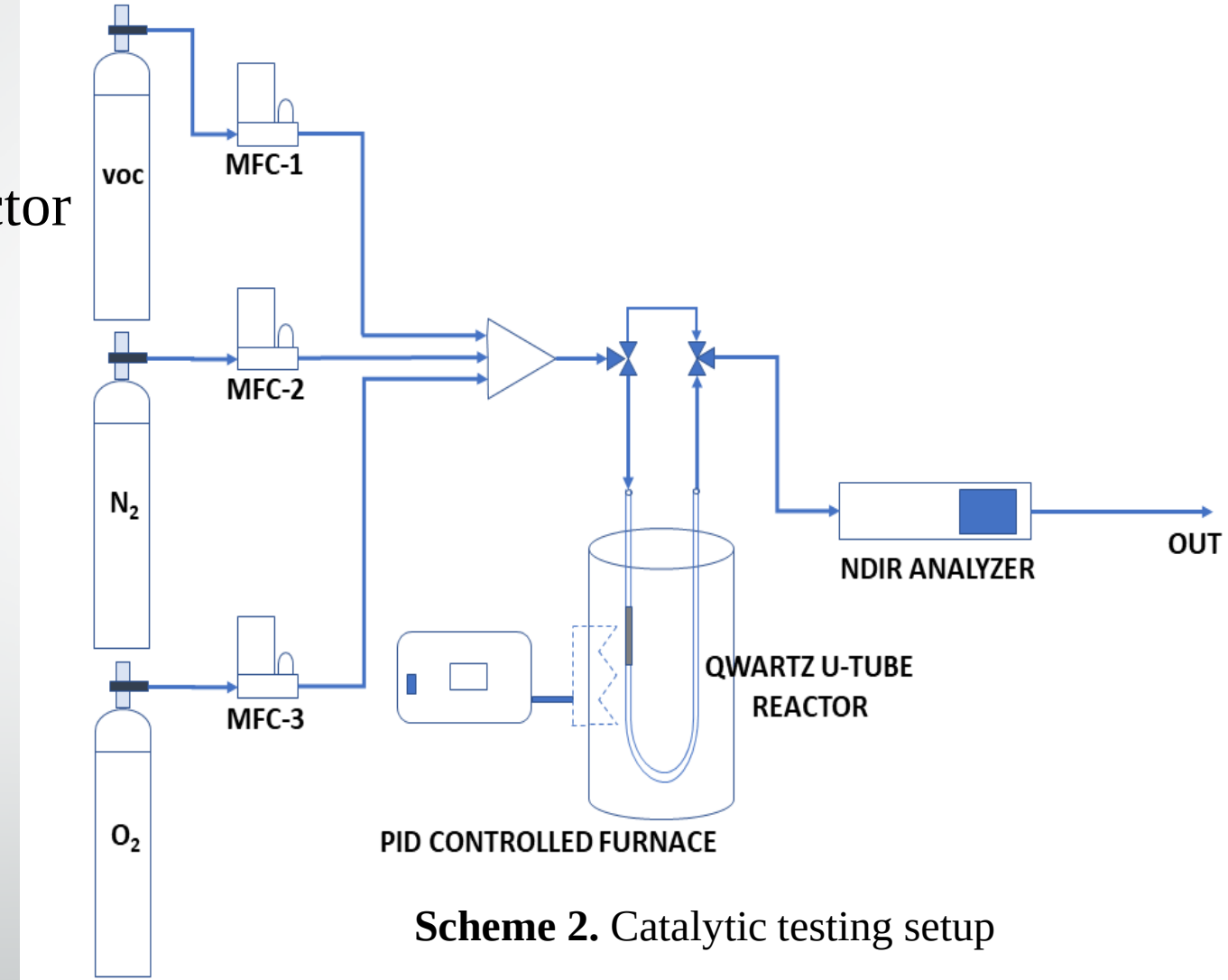
- Probe VOCs: Ethene, propene.
- Mass of catalyst: 0.1 g.
- Fixed bed quartz U-tube microreactor

Pretreatment

- N_2 flow rate: 50 NmL min^{-1}.
- 150 °C
- 1 hour

Testing

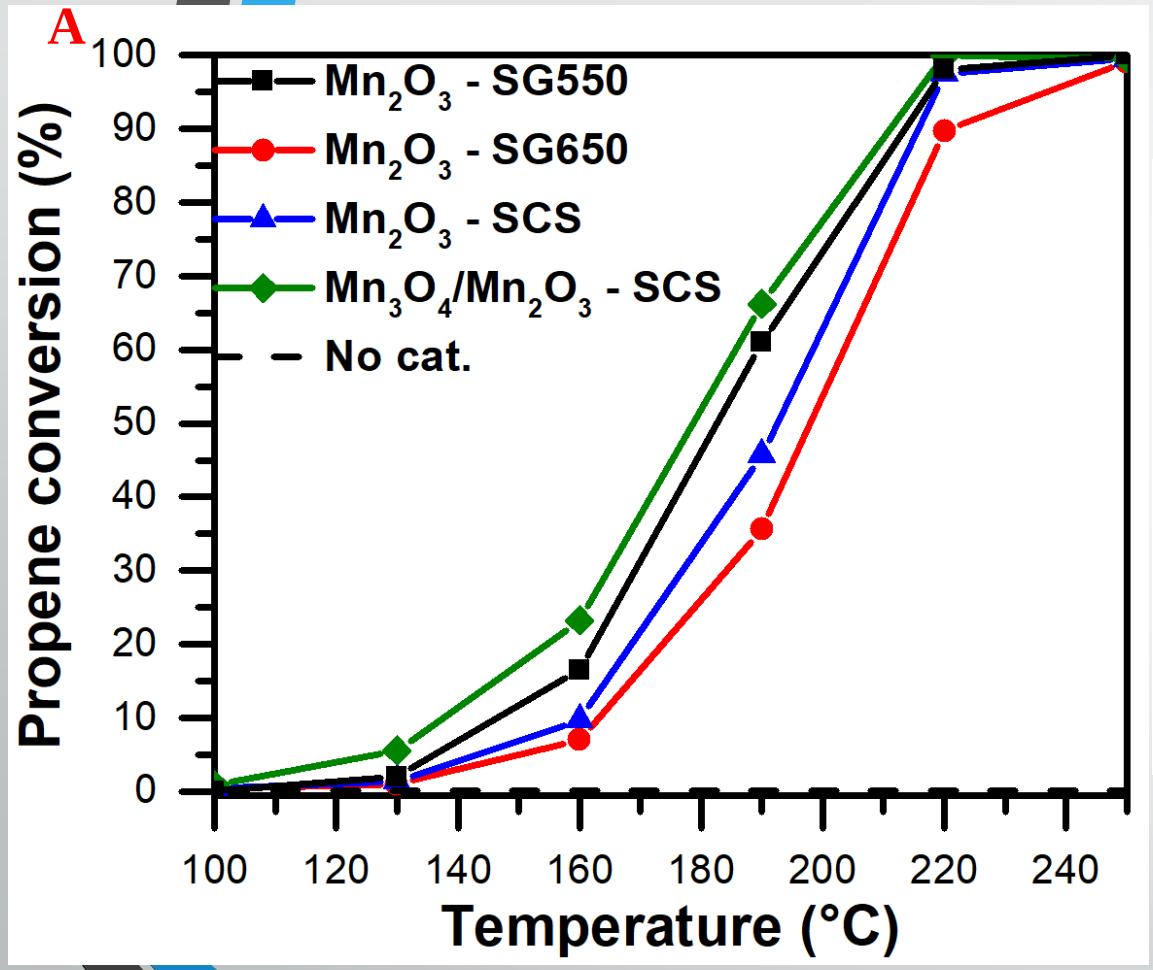
- Temperature range 100-280 °C.
- O_2 concentration: 10%.
- VOC concentration: 500 ppm.
- Gas hourly space velocity (GHSV): 20000 h^{-1}.
- W/F = 0.044 g h L^{-1}



Scheme 2. Catalytic testing setup

Catalytic Tests: VOC oxidation

Propene



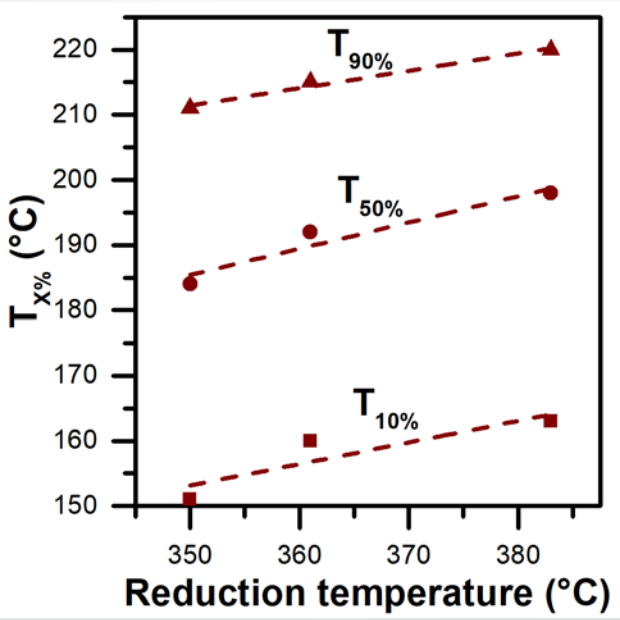


Figure 7. Catalytic performances in the oxidation of C_3H_6 (section A) and correlation between the low-temperature reduction peak and the catalytic performance in propene oxidation (over Mn_2O_3 catalysts) in terms of $T_{10\%}$, $T_{50\%}$ and $T_{90\%}$ (section B).

A direct correlation between the first reduction temperature and the catalytic performances (in terms of $T_{X\%}$) was verified for the Mn_2O_3 catalysts: the catalytic activity improved when the first reduction occurred at lower temperatures. Probable improved oxygen mobility [2,3]

Table 3. Propene specific reaction rates over the prepared catalysts.

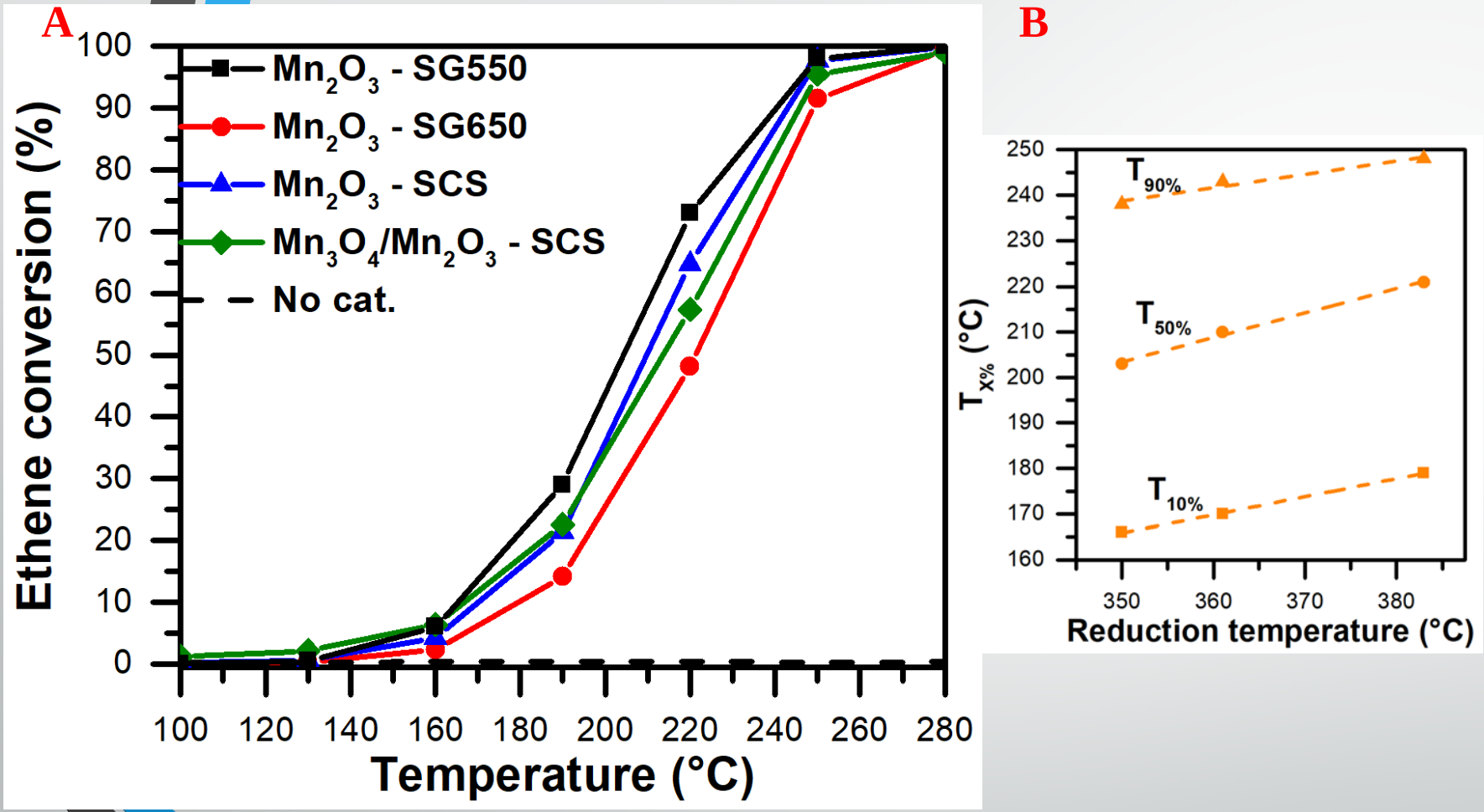
Catalyst	$r_{propene}$ [a] (µmol h^{-1} m^{-2})
Mn_2O_3-SG550	0.94
Mn_2O_3-SG650	0.49
Mn_2O_3-SCS	0.35
Mn_3O_4/Mn_2O_3-SCS	1.48

[a] calculated at 130 °C

[2] M. Piumetti, S. Bensaid, T. Andana, N. Russo, R. Pirone, D. Fino, Cerium-copper oxides prepared by solution combustion synthesis for total oxidation reactions: From powder catalysts to structured reactors, Appl. Catal. B Environ. 205 (2017) 455–468. https://doi.org/10.1016/j.apcatb.2016.12.054
[3] M.J. Marin Figueredo, T. Andana, S. Bensaid, M. Dosa, D. Fino, N. Russo, M. Piumetti, Cerium–Copper–Manganese Oxides Synthesized via Solution Combustion Synthesis (SCS) for Total Oxidation of VOCs, Catal. Letters. 150 (2020) 1821–1840. https://doi.org/10.1007/s10562-019-03094-x

Catalytic Tests: VOC oxidation

Ethene



As observed for propene oxidation, a correlation between the first reduction temperature and the catalytic performances (in terms of $T_{X\%}$) could be drawn for the Mn_2O_3 catalysts.

Table 4. Ethene specific reaction rates over the prepared catalysts.

Catalyst	r_{ethene} [b] (µmol h^{-1} m^{-2})
Mn_2O_3-SG550	1.67
Mn_2O_3-SG650	1.13
Mn_2O_3-SCS	1.04
Mn_3O_4/Mn_2O_3-SCS	1.69

[b] calculated at 160 °C

Figure 8. Catalytic performances in the oxidation of C_2H_4 (section A) and correlation between the low-temperature reduction peak and the catalytic performance in ethene oxidation (over Mn_2O_3 catalysts) in terms of $T_{10\%}$, $T_{50\%}$ and $T_{90\%}$ (section B).

Catalytic Tests: Carbon soot

- Fixed-bed composition:
  - Catalyst: 45 mg
  - Inert SiO_2: 150 mg.
  - Soot (Printex-U): 5 mg.
- Quartz U-tube microreactor

Pretreatment

- N_2 flow rate: 100 NmL min^{-1}.
- 100 °C
- 30 min

Testing

- Temperature range 200-700 °C.
- Flow rate: 100 NmL min^{-1}
- O_2 concentration: 10%.
- GHSV: 47700 h^{-1}.

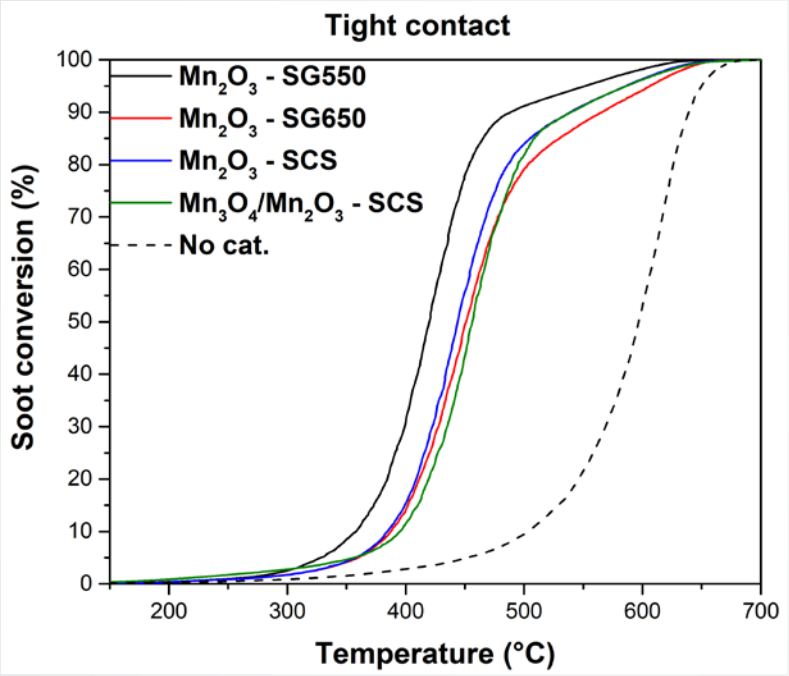


Figure 9. Catalytic conversion of carbon soot as a function of the temperature in "loose" contact conditions

High calcination temperatures probably **diminished the overall number of soot-MnO_x contact points** present in the catalysts. As well, **elevated amount of O_α species enhance the oxidation**. [4,6]

The spinel Mn_3O_4 overcomes the catalytic performance of the Mn_2O_3 – SG550, evidencing that the contact points soot-Mn_3O_4 enhance the catalytic performance: **morphology effect + (probable) high amount of acid sites over Mn_3O_4** [4,5]

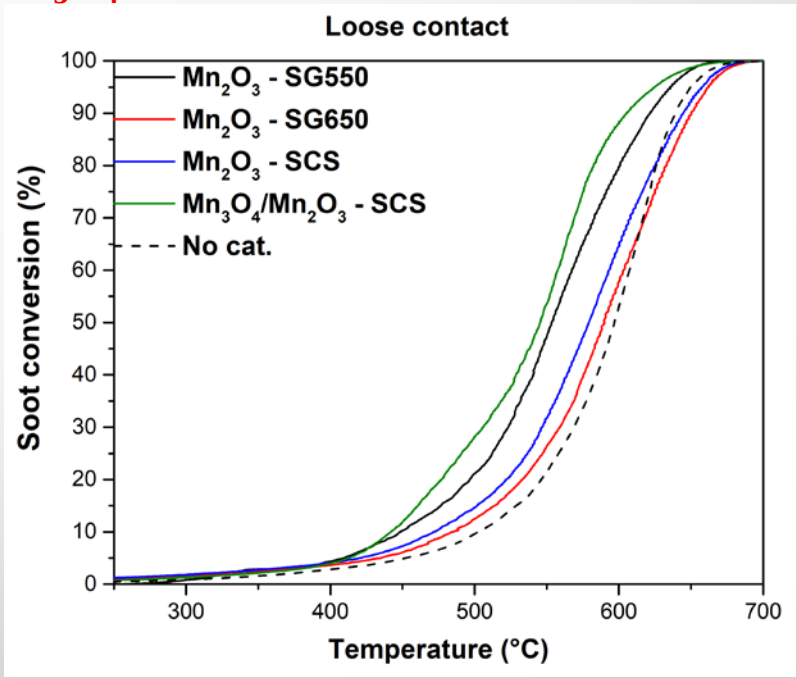


Figure 10. Catalytic conversion of carbon soot as a function of the temperature in "tight" contact conditions

[4] M. Piumetti, D. Fino, N. Russo, Mesoporous manganese oxides prepared by solution combustion synthesis as catalysts for the total oxidation of VOCs, Appl. Catal. B Environ. 163 (2015) 277–287. https://doi.org/10.1016/j.apcatb.2014.08.012.
[5] F.A. Deorsola, S. Andreoli, M. Armandi, B. Bonelli, R. Pirone, Unsupported nanostructured Mn oxides obtained by Solution Combustion Synthesis: Textural and surface properties, and catalytic performance in NOx SCR at low temperature, Appl. Catal. A Gen. 522 (2016) 120–129. https://doi.org/10.1016/j.apcata.2016.05.002
[6] D. Fino, S. Bensaid, M. Piumetti, N. Russo, A review on the catalytic combustion of soot in Diesel particulate filters for automotive applications: From powder catalysts to structured reactors, Appl. Catal. A Gen. 509 (2016) 75–96. https://doi.org/10.1016/J.APCATA.2015.10.016.

Conclusions

- The synthesis procedures allowed the preparation of catalysts with different physico-chemical and catalytic properties.
- The best catalytic performances in the abatement of solid carbon soot and VOCs, were observed in the Mn_2O_3 – SG550 and the Mn_3O_4/Mn_2O_3-SCS catalysts.
- The catalytic oxidation of VOCs was correlated to:

  (i) The elevated relative amounts of active surface O_α species

  (ii) The improved low-temperature reducibility of the catalysts

  (iii) The appearance of small crystallites

- The catalytic oxidation of soot was associated to:

  (i) In “tight” contact conditions, to the elevated relative amounts of O_α species and the improved low-temperature reducibility of the catalysts

  (ii) In “loose” contact conditions, to the combined effect of a filter-like morphology and a probable high amount of surface acid sites, characteristic of Mn_3O_4 catalysts

Acknowledgments

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Thanks for your attention!