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Synthesis of highly dispersed MnCeO$_x$ catalysts *via* a novel "redox-precipitation" route

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Abstract

A new synthesis route driving redox-precipitation reactions among Mn^{VII}, Ce^{III} and Mn^{II} precursors in basic aqueous solution yields MnCeO$_x$ catalysts (Mn loading, 9–33 wt%) with improved textural and structural properties in comparison to the conventional co-precipitation technique. Irrespective of the Mn loading, BET, X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) findings prove that the new method ensures a very high reproducibility in all the main physico-chemical properties of MnCeO$_x$ catalysts. Enabling a *monolayer dispersion* of the active phase, the "redox-precipitation" method greatly promotes the reducibility and the *surface affinity* of the MnCeO$_x$ system towards gas-phase oxygen.
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1. Introduction

Environmental catalysis is a rapidly growing field of both academic and technological interest pressed by the urgent need to preserve natural resources and human health. On this account a variety of catalytic processes for removing noxious organic pollutants in both gas-exhausts and wastewaters, mostly based on total oxidation reactions, are actually under scrutiny worldwide.

Although uncommon targets and reaction conditions do not allow assessing general rules on environmental catalysts requirements yet, according to theoretic principles of oxidation catalysis [1,2], an easy mobility and availability of oxygen at the catalyst surface constitutes the necessary condition for an effective conversion of organic substrates into carbon dioxide.

Potential alternative to high-cost noble-metal catalysts commonly employed in total oxidation processes [1–5], the MnCeO$_x$ system has attracted, since several decades, a great deal of research interest due to its noticeable performance in the catalytic wet oxidation of wastewaters with oxygen (CWO) [3–12], the catalytic combustion of VOC's [13–20] and the conversion/decomposition of NO$_x$ [21,22]. A superior catalytic activity is generally associated with an enhanced "reducibility" of "highly dispersed" manganese ions [4–13,16,20–23], while the reversibility of the redox

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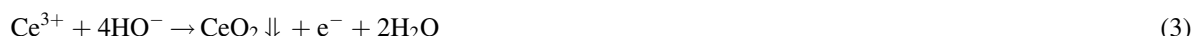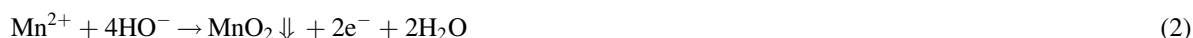*E-mail address:* Francesco.Arena@unime.it (F. Arena).

cycle involving surface manganese/ceria ions is critical for catalyst stability [6–9,14]. A proper "tuning" of textural, structural, and electronic features of the active phase has been then indicated as a benchmark for improving the reactivity of MnCeO$_x$ systems [4–11,20–23].

Therefore, this paper is aimed at probing that an original synthesis route driving *redox-precipitation* reactions among Mn and Ce precursors in basic solution leads to *monolayer-dispersed* MnCeO$_x$ catalysts in a very wide range (9–33 wt%) of the manganese loading. With a very high reproducibility, the redox-precipitation method allows improving the physico-chemical properties and the redox pattern of MnCeO$_x$ catalysts in comparison to the conventional co-precipitation technique.

2. Experimental

2.1. Catalysts

MnCeO$_x$ catalysts with different Mn-to-Ce atomic ratio (Mn$_{at}$/Ce$_{at}$, 0.33–2.1) were prepared *via* the novel "*redox-precipitation*" route, according to the following procedure. An amount of the KMnO$_4$ precursor in deionized water was titrated at ca. 333 K under vigorous stirring with an aqueous solution containing both Ce(NO$_3$)$_3$ and Mn(NO$_3$)$_2$ precursors. Keeping constant pH (8.0 ± 0.3) by the addition of a 0.2 M KOH solution, it has been ascertained that the following redox reactions:

$$MnO_4^- + 3e^- + 2H_2O \rightarrow MnO_2 \Downarrow + 4HO^- \tag{1}$$

$$Mn^{2+} + 4HO^- \rightarrow MnO_2 \Downarrow + 2e^- + 2H_2O \tag{2}$$

$$Ce^{3+} + 4HO^- \rightarrow CeO_2 \Downarrow + e^- + 2H_2O \tag{3}$$

occur in a quantitative way. With a lower limit of the Mn$_{at}$/Ce$_{at}$ ratio equal to 0.33 (e.g., mol$_{Mn}{}^{II}$ = 0), the designed catalyst composition was obtained dosing the various precursors according to the following quantitative relationships

$$3\,mol_{Mn^{VII}} = 2\,mol_{Mn^{II}} + mol_{Ce^{III}} \tag{a}$$

$$\frac{mol_{Mn^{VII}} + mol_{Mn^{II}}}{mol_{Ce^{III}}} = \left(\frac{Mn_{at}}{Ce_{at}}\right)_{design} \tag{b}$$

$$mol_{Mn^{VII}} + mol_{Mn^{II}} + mol_{Ce^{III}} = 1, \tag{c}$$

referred to electron (a) and mass (c) balance and catalyst composition (b), respectively. After titration, the solid was further digested for 30 min and then filtered, repeatedly washed with hot distilled water and dried overnight at 373 K. Aliquots of the dried samples were further calcined in air at 673 K (6 h).

A reference MnCeO$_x$ catalysts (Mn$_{at}$/Ce$_{at}$, 1.0) was prepared by the co-precipitation route using MnCl$_2$ and CeCl$_3$ (M1C1-P4) precursors and a 10 wt% Na$_2$CO$_3$ solution as precipitant [6–10,14,23]. After precipitation, the solid was dried at 373 K and then calcined in air at 673 K (6 h).

The list of the studied samples with the relative physico-chemical properties is given in Table 1.

Table 1
List of the studied catalysts

Catalyst	Mn$_{at}$/Ce$_{at}$[a]		[Mn] (wt%)	Preparation method	SA$_{BET}$ (m^2/g)	P.V. (cm^3/g)	A.P.D.[b] (Å)
	Des.	Exp.					
M1C3-R4	0.33	0.33	9.0	Redox-precipitation	148	0.25	54
M3C4-R4	0.75	0.71	16.7	Redox-precipitation	169	0.40	95
M1C1-R4	1.00	0.95	20.5	Redox-precipitation	154	0.44	111
M3C2-R4	1.50	1.44	26.7	Redox-precipitation	157	0.39	99
M2C1-R4	2.00	2.13	32.8	Redox-precipitation	150	0.46	131
M1C1-P4	1.00	0.94	20.4	Co-precipitation	101	0.24	94

[a] Atomic ratio from design and XRF analysis, respectively.
[b] Average pore diameter (4 P.V./SA$_{BET}$).