

Physico-chemical and catalytic properties of effective *nanostructured* MnCeO_x systems for environmental applications

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Abstract

A synthesis route based on the occurrence of redox reactions between Mn^{VII}, Mn^{II} and Ce^{III} precursors leads to nanostructured MnCeO_x systems with high surface area (120-250 m²/g) and a quasi-atomic dispersion of the active phase. Larger accessibility and higher oxidation state enhance the redox activity of the surface active Mn sites resulting in an improved mobility and availability of surface oxygen that greatly promotes the CO oxidation activity of the MnCeO_x system at low temperature (20-150°C).

Keywords: oxide catalyst; nanostructure; dispersion; oxygen mobility; redox activity

1. Introduction

The increasing levels of industrial pollution is pressing worldwide a great research concern on catalytic technologies for the abatement of noxious organic pollutants in gas-exhausts and wastewaters, mostly based on total oxidation reactions. Although uncommon targets and reaction conditions hinder the assessment of general rules for catalysts requirements yet, according to principles of oxidation catalysis an enhanced mobility and availability of oxygen at the catalyst surface constitutes the basic condition for an effective conversion of organic substrates to carbon dioxide [1]. This explains the exploitation of noble-metal catalysts [1-3], whose high cost remains the main drawback before an extensive development of environmental catalytic processes.

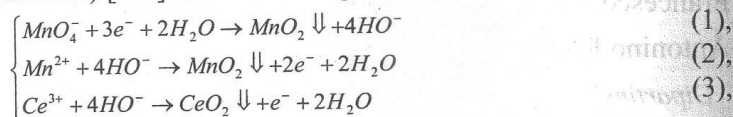
On this account, a great deal of research concern has been focused onto MnCeO_x systems, as a viable less-costly alternative to noble-metal catalysts [1,2]. However, the preparation method is crucial for tuning the catalytic behaviour of the title system, since high surface exposure and higher oxidation state of the active Mn sites are the main catalyst requirements [1-5]. Therefore, in an attempt to improve the total oxidation catalytic performance, we designed an alternative synthesis route of the MnCeO_x system based on *redox* reactions of suitable oxide precursors [1-5]. In fact, larger surface exposure and oxide dispersion promote the reducibility and the oxidative strength in comparison to the conventional co-precipitation method [1-5].

Therefore, this work shows some fundamental results documenting that the *nanosized* arrangement of the oxide domains in a wide range of the Mn loading (9-33 wt%) confers a superior electron and oxygen mobility to *redox* MnCeO_x systems, enhancing the reactivity at low temperature (20-150°C) in the CO oxidation, taken as a "model" reaction.

2. Experimental

2.1. Catalysts

MnCeO_x catalysts with different Mn-to-Ce atomic ratio (Mn/Ce) ranging between 0.33 and 2 were prepared via the “redox” route, consisting in the titration of a KMnO₄ solution at ca. 60°C under stirring with an aqueous solution of Ce(NO₃)₃ and Mn(NO₃)₂ precursors at constant pH (8.0±0.2) [1-5]. The following main redox reactions:



account for the “sticking” of the MnO_x and CeO_x phases at a quasi-molecular level, due to the required contact of Mn and Ce ions for the electron-transfer prompting the precipitation of both oxide species [3,4]. A reference MnCeO_x catalyst (Mn/Ce, 1.0) was obtained via the co-precipitation route of the MnCl₂ and CeCl₃ precursors [1-5]. All the solids were dried at 100°C and further calcined in air at 400°C (6h).

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

Table 1. List of the catalysts and main physico-chemical properties.

Catalyst	prep. meth.	Mn/Ce	[Mn] (wt%)	SA (m ² /g)	PV (cm ³ /g)	APD (nm)
M1C3-R	redox	0.34	9.3	168	0.28	5.1
M1C1-R	redox	0.95	20.5	154	0.49	11.7
M3C2-R	redox	1.44	26.6	157	0.45	14.3
M2C1-R	redox	2.12	32.7	140	0.50	16.7
M1C1-P	co-prec.	1.00	21.2	101	0.24	9.4

2.2. Methods

The physico-chemical characterization was carried out by BET, XRD, XPS, H₂-TPR (5% H₂/Ar) and CO-TPR (5% CO/He) techniques, while the CO oxidation activity was probed in the range of 100-150°C under kinetic regime by feeding a CO/O₂/He reaction mixture in the molar ratio of 2/1/22, at the rate of 0.1 stp L/min on powdered catalyst samples (0.035 g), diluted with granular SiC in the weight ratio of 1/10.

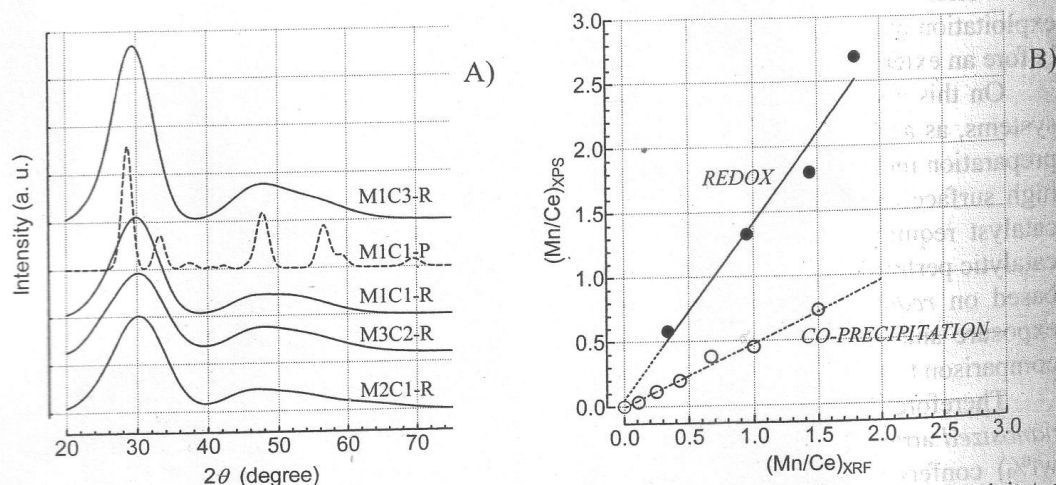


Figure 1. (A) XRD patterns and (B) surface chemical composition (XPS) of redox and co-precipitated MnCeO_x catalysts.

3. Results and discussion

The physico-chemical characterization data in Table 1 show a strong enhancement in the texture of the redox catalysts, evidenced by surface area (SA) and pore volume (PV) values much larger than those of the co-precipitated one [1-5]. At variance of the co-precipitated system, showing the diffraction lines of cerianite and, to a lower extent of pirolusite [1,4], the XRD data (Fig. 1A) of the redox systems show analogous featureless patterns, irrespective of the composition. This indicates that the improved catalyst texture reflects the lack of any "long-range" crystalline order, as a consequence of the quasi-molecular mixing of the oxide phases, hindering the formation and growth of whatsoever crystalline domains [1,3]. This peculiar architecture also accounts for the quite regular pore size distribution [1-3] and the tinier average pore diameter (APD) of the redox systems (Table 1). Notably, further evidences on the homogeneity of the redox catalysts at microscopic level are provided by XPS data in Figure 1B. In spite of the high loading (9-33 wt%), the oxide dispersion keeps constant in the whole Mn/Ce ratio range, resulting even in a considerable surface enrichment of the active phase never observed for the co-precipitated systems [1]. This still depends on the singular characteristics of synthesis route that enables very effective reciprocal oxide dispersion [1-4] and, consequently, a strong synergism between ceria carrier and the active phase. Such an effective interaction promotes the electron transfer processes enhancing the oxygen mobility and the oxygen activation functionality at low temperature [1-3]. This is evident from TPR patterns under both H₂ and CO, shown in Figure 2. The superior rate of H₂ consumption at T < 200°C (Fig. 2A) signals immediately the greater oxygen mobility and availability of redox catalysts [1-3]. Furthermore, a peak at ca. 130°C, not observed for the co-precipitated sample, parallels a larger intensity and downshift of the main reduction components. The superior reactivity of CO prompts the reduction of the redox systems already at 20°C, resulting in a systematic downshift of all the peaks (Fig. 2B), while the component at ca. 130°C observed under H₂ (Fig. 2A) is no longer visible.

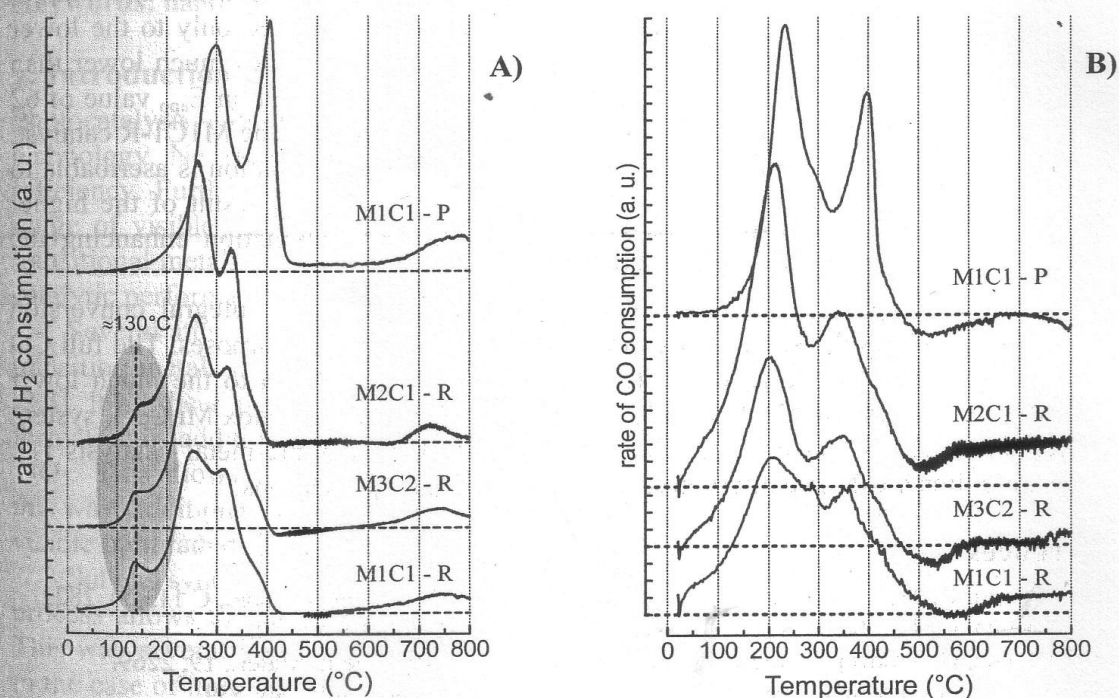


Figure 2. TPR patterns of the catalysts under H₂ (A) and CO (B) after a pre-treatment in situ at 400°C in flowing oxygen.

This confirms that the latter component arises from very reactive electrophilic oxygen species, formed by the activation of molecular oxygen during the *in situ* pre-treatment [1-4] and driving the CO oxidation at 20°C during the baseline stabilization. This enhanced reactivity toward CO at low temperature of the redox systems, paralleling the activity in the wet air oxidation of phenol [2], prompted the comparison of the oxidation behavior of the homologous M1C1-R and M1C1-P samples. The results of the catalytic tests are presented in Table 2 in terms of CO conversion (X_{CO}), reaction rate, site time yield of Mn sites (sty_{Mn}) and apparent activation energy.

Table 2. Kinetic and integral CO oxidation data of the M1C1-R and M1C1-P catalysts.

Catalyst	T (°C)	$^aX_{CO}$ (%)	reaction rate ($\mu\text{mol}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{s}^{-1}$)	sty_{Mn} (s^{-1})	E_{app} (kJ/mol)
M1C1-R	100	1.6	2.9	7.6E-4	43±4
	130	3.9	6.9	1.9E-3	
	150	8.2	14.2	3.8E-3	
	150	97.1 *			
M1C1-P	130	0.3	0.9	2.4E-4	62±3
	140	0.7	1.3	3.4E-4	
	150	1.1	2.0	5.1E-4	
	150	37.6 *			

* integral conversion values obtained in the following conditions: w_{cat} 0.3 g; F , 0.05 stp L/min; $CO/O_2/He=1/5/94$.

The superior reactivity of the redox system is immediately evident from systematically higher CO conversion values under kinetic and integral conditions. In fact, the M1C1-R catalyst features a noticeable activity in the range of 100-150°C with rate values rising from ca. 3 to 15 $\mu\text{mol}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{s}^{-1}$, comparables with those of metal systems [1]. On the other hand, much lower conversion and rate values confirm the weaker oxidation strength of the M1C1-P catalyst, which cannot be related only to the lower availability of active Mn sites. Indeed, specific rate and sty_{Mn} values much lower than the ca. threefold lower active phase dispersion (Fig. 1B) account for an E_{app} value of 62 kJ/mol, considerably higher than the 43 kJ/mol value recorded for the M1C1-R catalyst. Such a difference in the value of the energetic barrier for CO oxidation is ascribable to the easier generation of active *electrophilic* oxygen species, as a result of the higher oxide dispersion and the consequent stronger MnO_x - CeO_2 interaction enhancing the electron-transfers process(es) at the catalyst surface [1,3].

Then the reactivity in the CO oxidation was probed under integral conversion conditions to address the suitability of the system for applicative purposes. The full CO conversion attained by the redox system at 150°C, in comparison to the much lower value (ca. 38%) of the M1C1-P sample, supports the fact that the redox $MnCeO_x$ system features an oxidative performance comparable with that of noble-metal catalysts [1], constituting thus a valuable alternative for environmental applications.

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