Probing the functionality of *nanostructured* MnCeO$_x$ catalysts in the carbon monoxide oxidation
Part II. Reaction mechanism and kinetic modelling

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ABSTRACT

The kinetics of the CO oxidation on a typical *nanocomposite* MnCeO$_x$ catalyst (M5C1) were probed by temperature programmed catalytic reaction (TPCR) tests in the range of 293–533 K, varying reagent partial pressure (*i.e.*, p_{CO} and p_{O2}) between 0.00625 and 0.025 atm (P, 1 atm) (Arena et al., 2017). Experimental data indicate kinetic orders of 0.6 and 0.4 on p_{CO} and p_{O2} respectively, with apparent activation energy of 40 ± 3 kJ/mol (Arena et al., 2017). A systematic study of the interaction pattern of catalyst with reagent and product molecules shows easy reactivity of surface oxygen to CO, low mobility of lattice oxygen and weak surface affinity to CO$_2$. Systematic evidences on reaction mechanism and surface intermediates signal an *extrafacial* redox path, triggered by abstraction of oxygen atoms in the neighbouring of active Mn^{IV} sites (Arena et al., 2017), and sustained by O$_2$ species adsorbed on those surface oxygen vacancies. A Langmuir-Hinshelwood (L-H) reaction mechanism leads to a formal kinetic model explaining the CO oxidation functionality of bare and promoted MnO$_x$ catalysts.

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1. Introduction

Despite a huge research interest focused during last decades on low-cost transition metal oxide (TMO) catalysts, nowadays many environmental catalytic technologies rely on the total oxidation functionality of supported noble-metals, driving the combustion of pollutants in gas and liquid exhausts [2–5]. Among countless model compounds useful to assess the efficiency of new catalyst formulations, carbon monoxide is matter of practical and scientific concerns as it is a highly toxic species for living beings and a precursor of tropospheric ozone, being also a poison for important catalytic technologies (*e.g.*, Ammonia, Fuel Cells, *etc.*). Furthermore, its oxidation is one of the simplest model reactions, commonly employed

in surface science and catalytic studies, to probe the functionality of metal and TMO catalysts [1,2,5].

Beside to the well-known reactivity of supported noble-metals, cobalt-based catalysts are active even at sub-ambient conditions but suffering from relevant deactivation phenomena [5–7], while bare and promoted MnO$_x$ materials exhibit a good CO oxidation performance in low-medium temperature windows (293–573 K) [1,3,5,8–27]. In particular, composite MnCeO$_x$ systems represent a viable alternative to noble-metals for the mineralization of pollutants in gas and liquid phases, although the synthesis method controls physico-chemical and catalytic properties [3,11,17]. Then, despite remarkable structural effects promote surface exposure, dispersion and reducibility of *nanostructured* MnCeO$_x$ materials [1,3,8,11,17,20–22,27], larger availability of surface active Mn^{IV} sites explains the higher reactivity of the bare MnO$_x$ system in the CO oxidation [1], and the selective aerobic oxidation of benzyl alcohol [27].

It is recognised that conventional supported noble-metals drive a Langmuir-Hinshelwood (L-H) reaction path, accounting for the inhibitory effect of CO and the higher reactivity (*i.e.*, TOF) of large metal particles, while in combination with ceria carrier a dual-site mechanism prevails [5]. At variance, under high O$_2$ pressure

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conditions platinum catalysts form a surface oxide layer enabling the stepwise Mars van Krevelen (MvK) redox path [28]. On the other hand, the mechanism for CO oxidation on TMO catalysts is still undefined [2,5,9,11–18,21–24,29], and attempts of kinetic modelling are, thus, fairly sporadic [30,31]. Mechanistic clues are consistent with a L-H path also for bare and promoted MnO_x catalysts [11–18,22–24], while empiric correlations between catalyst reducibility and activity could argue the MvK route [5,16,21,31]. In fact, recent computational studies on model Mn-doped ceria systems predict an easy reactivity of surface Mn—O—Ce bonds and the consequent formation of oxygen vacancies generating, in turn, very reactive diatomic specie (*e.g.*, O_2-, $O_2=O_2-$, $O_2=$) under reaction conditions [23,24]. Moreover, IR spectroscopy provides evidence of various intermediates formed by CO at the surface of bare and promoted MnO_x catalysts, even at low temperature and in absence of O_2 [15,21,22,26].

Therefore, after documenting the effects of Ce addition on physico-chemical properties and CO oxidation activity of *nanostructured* $MnCeO_x$ systems, along with an unchanging reaction mechanism driven by surface Mn^{IV} active sites in the range of 293–533 K, this work addresses kinetic and mechanistic issues of the CO oxidation on a typical *nanostructured* $MnCeO_x$ catalyst (*i.e.*, M5C1) [1]. Kinetic data in the range of 293–403 K and systematic evidences on the interaction pattern of the catalyst with reagent and product molecules are synthesised into a L-H mechanism and a formal kinetic model predicting the CO oxidation functionality of bare and promoted MnO_x catalysts.

2. Experimental

2.1. Catalysts preparation

The M5C1 catalyst (Mn_{at}/Ce_{at}, 5) was synthesized *via* the previously described *redox-precipitation* method [1,27], consisting in the titration of the $Mn(NO_3)_2 \cdot 4H_2O$ (>97%, *Carlo Erba*) precursor by an aqueous solution (0.15 L) of $KMnO_4$ (≥99%, *Carlo Erba*) and $Ce(NH_3)_2(NO_3)_6$ (>98.5%, *Aldrich*) precursors, at constant pH (4.5 ± 0.5) [32,33]. The M5C1 catalyst has surface area, pore volume, and average pore diameter of $160 \, m^2/g$, $0.55 \, cm^3/g$ and 30 nm, respectively [1]. Before measurements, the catalyst samples were pretreated *in situ* under a 5% O_2/He flow at 423 K for 1 h.

2.2. Catalyst characterization

Temperature Programmed Reduction (CO-TPR) measurements in the range of 293–773 K were carried out in a conventional apparatus operating in both continuous and pulse mode, using a 5% CO/He carrier flowing (60 stp mL min^{-1}) in a quartz micro-reactor (i.d., 4 mm) heated at the rate of 12 K/min (w_{cat}, 20 mg) [1].

Temperature Programmed Desorption (TPD) measurements were carried out in the above apparatus, using He as carrier gas (60 *stp* mL min^{-1}) and a heating rate of 12 K/min. Pretreated catalyst samples (20 mg) were cooled at r.t. (298 K) and further treated under 5% CO/He, CO/O_2/He ($p_{CO} = p_{O2}$, 0.025 atm) or 10% CO_2/He flow for 1 h. Thereafter, the catalyst was flushed by the carrier gas and, after baseline stabilization, the (m/z) signals of He (4), H_2O (18), CO (28), O_2 (32) and CO_2 (44) were recorded by a QMS (*Hiden Analytical,* HPR 20), operating in MID mode with the SEM amplifier at 1200 V [1].

Steady-state O_2 uptake measurements were performed in pulse mode after catalyst (20 mg) exposure to the He/CO/O_2 reaction mixture (CO/O_2, 0.25–3.3) at 393 K for 1 h. After flushing by the He carrier (35 *stp* mL min^{-1}), O_2 micro-pulses ($2.7 \cdot 10^{-9}$ mol$_{O2}$) were injected, with no consumption being recorded irrespective of the reaction mixture composition (*v. infra*).
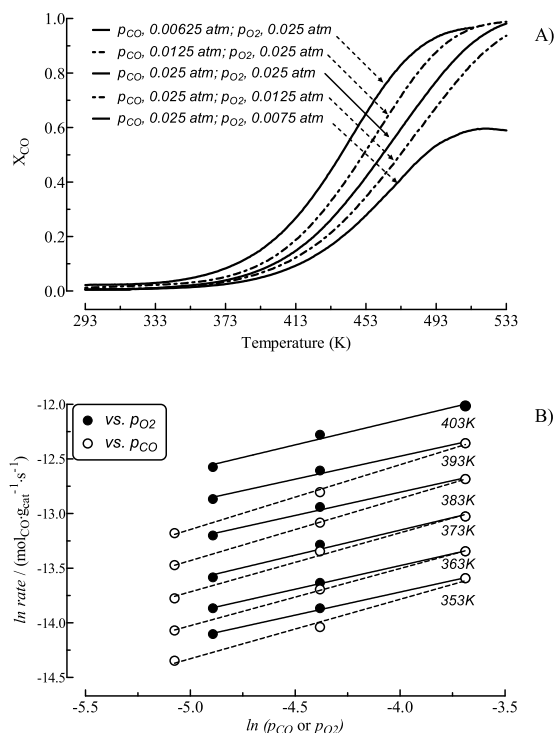
Fig. 1. (A) CO conversion of the M5C1 catalyst in the range of 293–533 K at different p_{CO} and p_{O2} (F, 60 stp mL/min; P, 1 atm; w_{cat}, 0.02 g); (B) log-plot of rate data in the range of 353–403 K (X_{CO} < 12%).

2.3. Catalyst testing

CO oxidation kinetic data in the range of 293–533 K were obtained by temperature programmed catalytic reaction (TPCR) tests, feeding a CO/O_2/He mixture at the rate of 60 *stp* mL min^{-1} (P, 1 atm), with p_{CO} and p_{O2} varying between 0.00625 and 0.025 atm (w_{cat}, 20 mg). The reaction stream was analysed *on line* by the QMS [1].

Pulse CO oxidation tests were carried out at 393 K injecting five consecutive CO pulses ($1.3 \, \mu mol_{CO}$) on the catalyst (20 mg) kept under 5% O_2/He carrier (35 *stp* mL/min) and, then, other five pulses under He flow. The CO and CO_2 signals were acquired by the QMS, as above described.

3. Results and discussion

3.1. Reaction kinetics and mechanistic evidences

3.1.1. Empiric kinetics

The kinetics of the CO oxidation on the M5C1 catalyst were probed varying the CO and O_2 pressure in the range of 0.00625–0.025 atm, to ensure "ideal" kinetic conditions and the absence of mass-transfer resistances in the whole conversion range [1]. Activity data at different p_{CO} and p_{O2} in Fig. 1A show a regular growth of CO conversion to final values comprised between 60 and 100% (533 K), the former depending on the limiting O_2 pressure at the highest p_{CO}/p_{O2} ratio (3.3). Moreover, conversion levels lowering with p_{CO} and rising with p_{O2} denote a kinetic dependence in-between 0 and 1 for both reagents, as confirmed by the log-plot of rate data in the range of 353–403 K (X_{CO} < 12%), indicating constant reaction orders of 0.6 and 0.4 with respect to p_{CO} and p_{O2}, respectively (Fig. 1B). Diagnostic of similar resistances for the activation of CO and O_2 molecules, such a kinetic dependence matches previous literature data for the CO oxidation on composite $MnCeO_x$ [11] and MnO_x catalysts [12–14].