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Design of Effective Ceria-supported MnO$_x$ Catalysts for the CWO of Phenol

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Abstract

The effects of preparation method, Mn loading and promoters (K and Pd) on the physico-chemical properties and phenol catalytic wet oxidation (CWO) activity of the MnCeO$_x$ system are addressed. Huge amounts of carbonaceous species at the surface of "spent" catalysts indicate that the CWO of phenol proceeds *via* a typical heterogeneous path, while the concomitance of catalyst reduction and phenol oxidation signal that surface reaction of adsorbed intermediate(s) with activated oxygen species is the *rate determining step (r.d.s.)*. Textural and redox properties are then key-requirements of design of improved MnCeO$_x$ catalysts for the CWO of phenol.

1. INTRODUCTION

Amongst various methods claimed as effective for the mineralization of wastewater streams, a special attention was focused in the last decades on the Catalytic Wet Oxidation (CWO) using either noble-metal or transition-metal-oxide catalysts [1]. Although Cu-based systems were claimed to be very effective CWO catalysts, it has been documented that their catalytic action stems from the leaching of the active phase driving an effective, yet homogeneous, reaction path [2-4]. Then, MnCeO$_x$ composite catalysts constitute to date the most viable alternative to noble-metal systems for detoxification of industrial wastewaters [1,4-6]. Addressing the effects of composition and promoters on the catalytic behaviour of the co-precipitated MnCeO$_x$ system, Larachi's group put emphasis on the superior performance of a K-doped (4 wt%) system in terms of activity and stability [4]. However, Abecassis-Wolfovich *et al*. recently showed that the phenol CWO activity of such systems can be in fact related to *surface reactive adsorption* (SRA) and *catalyst adsorption capacity* (CAC), while regeneration temperatures much higher than those of the CWO process are required for restoring the initial activity [5]. Contrarily to previous evidences attributing a better activity to higher average oxidation numbers of Mn ions [4,5], moreover they ascribed a superior CWO performance of the MnCeO$_x$ system to a Mn$_5$O$_8$ phase enhancing its oxidation strength [5].

Therefore, this paper is aimed at assessing the effects of preparation method and ⟨
composition on the CWO pattern of MnCeO$_x$ systems. Basic insights into the reaction mec⟨
provide evidence of a typical heterogeneous path pointing to enhanced surface texture (*adso*⟨
and oxygen mobility (*oxidation*) as key-requirements of MnCeO$_x$ systems for CWO reaction.⟨

2.   EXPERIMENTAL

2.1.   Catalysts

Several MnCeO$_x$ catalysts (Mn$_{at}$:Ce$_{at}$, 0.75-1.0) were prepared by co-precipitat⟨
Mn(NO$_3$)$_2$, CeCl$_3$ and Ce(NO$_3$)$_3$ precursors with a 10% Na$_2$CO$_3$ aqueous solution [4].⟨
filtration and washing, all the samples were dried at 373K (16h) and further calcined in air a⟨
(6h). K (4 wt%) and Pd (1 wt%) promoters were added by incipient wetness of the dried sa⟨
with KNO$_3$ and Pd(NO$_3$)$_2$ aqueous solutions respectively, following drying (373K) and calci⟨
(673K) treatments as above specified.

Table 1. List of the catalysts

Code	Mn$_{at}$:Ce$_{at}$	CeO$_2$ precursor	Promoter (wt%)	SA$_{BET}$ (m⟨
MC-1	3:4	Ce(NO$_3$)$_3$	-	66
MC-2	1:1	Ce(NO$_3$)$_3$	-	72
MC-3	1:1	CeCl$_3$	-	99
KMC-1	3:4	Ce(NO$_3$)$_3$	K (4)	27
KMC-3	1:1	CeCl$_3$	K (4)	61
PdMC-3	1:1	CeCl$_3$	Pd (1)	68

2.2.   Physico-Chemical Characterization

Surface area (SA$_{BET}$) values were obtained from nitrogen absorption isotherms (⟨
elaborated according to the BET method. *TPR* analyses (293-1073K) were run using a 6% ⟨
mixture (F, 60 *stp* mL min^{-1}) and a heating rate of 12K·min^{-1}. *TGA-DSC* analyses were perform⟨
a 10% O$_2$/He flow with a heating rate of 12K·min^{-1}, using a *Netzsch STA 409 C* analyzer coupl⟨
a Quadrupole Mass Spectrometer (*Fisons Instruments*) for continuous scanning of the outlet str⟨

2.3.   Catalyst Testing

Catalyst testing in the CWO of phenol at 110°C was performed in a semi-batch mode usi⟨
0.25 L stirred (≈1000 rpm) autoclave fed with pure oxygen (0.2 *stp* L·min^{-1}, p$_{O2}$, 8 atm). The i⟨
phenol concentration was set at 1,000 ppm while the catalyst load was fixed at 5,000 ppm (R, 5⟨
Liquid reaction samples were analyzed with respect to pH, phenol, TOC and Mn concentration [⟨

3.   RESULTS and DISCUSSION

Taking into account the effects of the preparation method and catalyst composition (Fig. ⟨
and promoters addition (Fig. 1B), the activity data of the various catalysts in the CWO of phe⟨
denote a significant performance evidenced by a complete phenol removal in a time compr⟨

between 15 (KMC-3 and PdMC-3) and 100 min (MC-1) while, with a similar trend, the TOC decrease ranges between 60 and 80%. Namely, the MC-1 system (Fig. 1A), characterized by the lower Mn_{at}/Ce_{at} ratio and SA_{BET} exposure is the less effective catalyst, though its performance is just slightly worse than that of the MC-2 sample, characterized by a higher manganese loading and SA value (Table 1). By contrast the bare $MnCeO_x$ system, obtained from the $CeCl_3$ precursor, exhibits a superior efficiency [1,4] proved by the attainment of a complete phenol removal after only 30 min. Despite of faster reaction kinetics, all the systems get final (after 2h) comparable levels of phenol elimination (≥90%) while that of TOC is generally lower. The addition of K or Pd [1,4,5] does not further improve the reaction kinetics of the most active MC-3 system, whereas K has an appreciable promoting effect on the performance of the less reactive MC-1 system (Fig. 1B). Since XRD analysis of the various systems do not provide evidence of significant differences in phase composition [6], textural and redox features must account for the different CWO pattern of the various systems [4-6]. Indeed, though the worse and better performances are related to the

Figure 1. Phenol (●,▲,◆) and TOC (○, △,◇) conversion vs. reaction time. A) Effect of preparation method and catalyst composition; B) effect of K and Pd addition on the activity of MC-1 and MC-3 catalysts.

lowest and largest SA_{BET} exposure (Table 1), it is not the only parameter affecting the CWO activity of the bare $MnCeO_x$ samples. Regardless of chemical composition, TGA-DSC data reveal on all the "spent" catalysts the presence of huge amounts of carbonaceous deposits, to an extent in any case corresponding almost quantitatively (15-17%) to the initial phenol/catalyst mass ratio (1/5), with the exception of the Pd-promoted system for which a weight loss of only 10% has been found [6]. These findings signal that the different conversion level is then related to the kinetics of the surface adsorption rather than to an effective mineralization of the substrate [5], as confirmed by minor changes in pH (7-9) of the reacting solution [2,3,6]. Thus, the CWO of phenol on $MnCeO_x$ systems proceeds *via* a "typical" heterogeneous path involving the first adsorption of the substrate (*step 1*) and its subsequent conversion into various intermediates and/or CO_x by the attack of activated oxygen species (*steps 2,3*), the last acting as *r.d.s.* of the overall reaction network [5]:
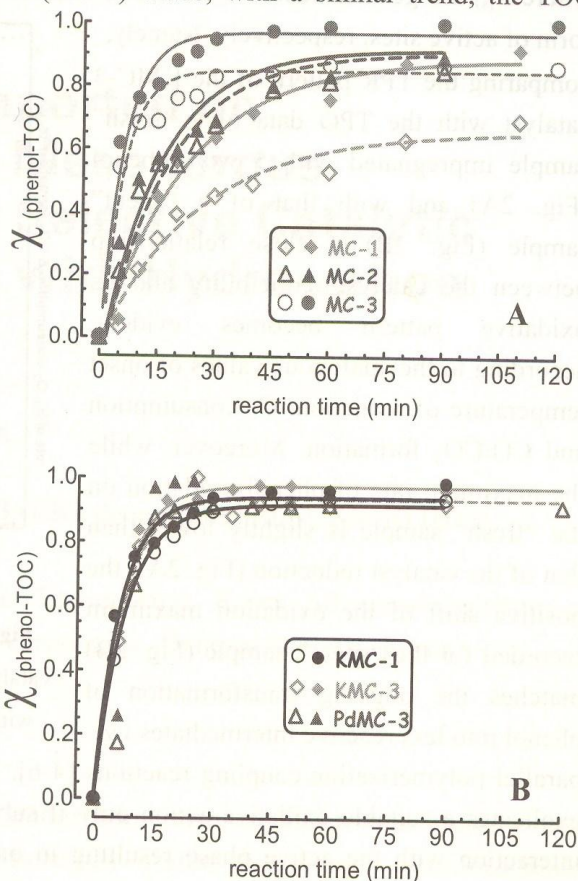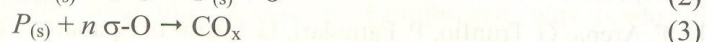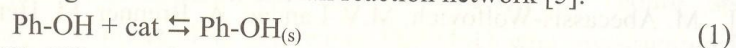
$$Ph\text{-}OH + cat \leftrightarrows Ph\text{-}OH_{(s)} \tag{1}$$
$$Ph\text{-}OH_{(s)} + \sigma\text{-}O \rightarrow P_{(s)} + \sigma \tag{2}$$
$$P_{(s)} + n\,\sigma\text{-}O \rightarrow CO_x \tag{3}$$
$$\sigma + O_2 \rightarrow \sigma\text{-}O \tag{4},$$

where $P_{(s)}$ are generic adsorbed intermediates, while "σ-O" and "σ" the oxidised and the reduced form of active sites, respectively. Namely, comparing the TPR pattern of the KMC-3 catalyst with the TPO data of a "fresh" sample impregnated with 5 wt% phenol (Fig. 2A) and with that of a "spent" sample (Fig. 2B) a close relationship between the catalyst reducibility and its oxidative pattern becomes evident, according to the analogous values of onset temperature of reduction, O_2 consumption and CO/CO_2 formation. Moreover, while the maximum rate of phenol oxidation on the "fresh" sample is slightly lower than that of the catalyst reduction (Fig. 2A), the positive shift of the oxidation maximum recorded for the "spent" sample (Fig. 2B) matches the ongoing transformation of phenol into less reactive intermediates *via*
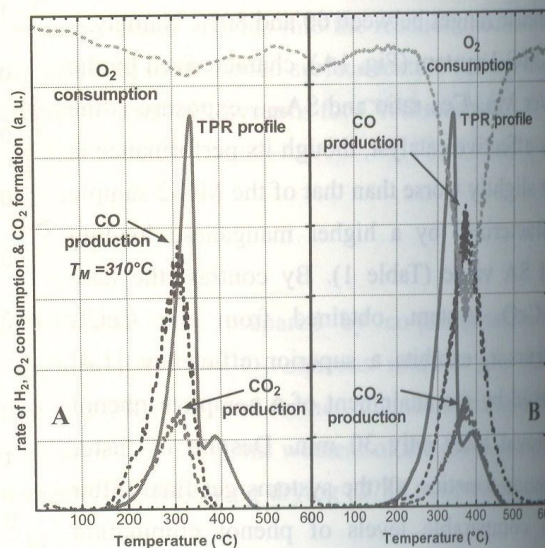

Figure 2. Comparison of the TPR spectrum of the KMC-3 catalyst with TPO patterns of a "fresh" sample impregnated with phenol (A) and with that of the "spent" sample (B).

parallel polymerization/coupling reactions [4-6]. These findings indicate that the MnCeO$_x$ system explicates a suitable oxidative action only if substrate and/or intermediates establish an effective interaction with the active phase resulting in oxygen-to-manganese electron transfer (*steps 2-3*) prompting a redox reaction cycle involving phenol oxidation and the subsequent/concomitant incorporation of gas-phase oxygen (*step 4*). In other words, the oxidation of phenol proceeds *via* a **"*redox*"** reaction path driven by an enhanced reducibility of the active phase prompting the activation of lattice oxygen into very reactive electrophylic species [5-7]. These evidences lead us to exploit a new synthesis route which, enhancing texture and redox features of the MnCeO$_x$ system [7], result in a considerably better performance in the CWO of phenol [6].

REFERENCES

[1] S.K. Bhargava, J. Tardio, J. Prasad, K. Foger, D.B. Akolekar, S.C. Grocott, Ind. Eng. Chem. Res.45 (2006) 1221.

[2] F. Arena, R. Giovenco, T. Torre, A. Venuto, A. Parmaliana, Appl. Catal. B 45 (2003) 51.

[3] F. Arena, E. Alongi, P. Famulari, A. Parmaliana, G. Trunfio, Catal. Lett. 107 (2006) 39.

[4] S.T. Hussain, A. Sayari, F. Larachi, J. Catal. 201 (2001) 153.

[5] M. Abecassis-Wolfovich, M.V. Landau, A. Brenner, M. Herskowitz, Ind. Eng. Chem. Res. 43 (2004) 5089.

[6] F. Arena, G. Trunfio, P. Famulari, G. Caprì, L. Spadaro, Catal. Lett. in preparation.

[7] F. Arena, G. Trunfio, J. Negro, G. Gatti, L. Spadaro, Chem. Mater. (2006) submitted.