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Basic evaluation of the catalytic pattern of the CuCeO$_x$ system in the wet oxidation of phenol with oxygen

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The working mechanism of a ceria-supported Cu (Cu$_{at}$:Ce$_{at}$ = 1:10) system in the Catalytic Wet Oxidation (CWO) of phenol with O$_2$ (T_R, 130–170 °C; P_{O2}, 7 atm) has been thoroughly assessed. Basic relationships amongst pH, extent of leaching and rate of phenol and TOC conversion prove the major contribution of a homogeneous catalytic path by Cu ions on the peculiar CWO pattern of supported copper catalyst. In addition, gas-phase reduction/oxidation tests signal the lack of reversibility of the redox cycle of the CuCeO$_x$ system under typical reaction conditions.

KEY WORDS: catalytic wet oxidation; phenol; Cu catalyst; reaction mechanism; leaching; homogeneous catalysis; pH; deactivation.

1. Introduction

During last decades a growing necessity to minimize pollutants' emissions of industrial liquid effluents has stimulated a great deal of fundamental and applied research interest aimed at disclosing alternative routes for an efficient *mineralization* of wastewater streams, incompatible with conventional biological decontamination treatments [1–3]. Amongst the various approaches proposed, the catalytic wet oxidation (CWO) with air represents nowadays one of the most promising technologies to attain an effective degradation of many classes of noxious and refractory pollutants [1–3]. Using mostly phenol [1–20] and acetic acid [1,2,21] as model compounds, it has been ascertained that noble metal catalysts feature an outstanding CWO performance, though undergoing relevant deactivation phenomena mainly induced by strong adsorption of carbonaceous deposits (*fouling/poisoning*) [1,2]. Moreover, also in the perspective of finding out less costly alternatives to precious metal catalysts, a rising scientific concern has been progressively forwarded onto transition metal oxide systems, getting a suitable CWO activity of Cu [6–13,21] and Mn [14–21] based systems towards several substrates under relatively mild reaction conditions. Nevertheless, *leaching* and/or *fouling* deactivation phenomena remain still the main drawbacks to overcome for a successful commercial application of the CWO technology [1–3,9–12,14–16,20–22].

Larachi and co-workers [14–16] primarily focused their research interest onto the MnCeO$_x$ system, stressing a strong influence of the redox features of the active phase on the CWO performance of differently loaded catalysts. Attempting to improve the performance of an optimized system (e.g., Mn$_{at}$:Ce$_{at}$ = 1) by various promoters (Pt, Pd, Ag, K, etc.), they found that potassium addition (4 wt.%) enhances both activity and resistance to fouling, allowing besides for a substantial mitigation of reaction conditions in the CWO of phenol [17–20].

After the basic studies of Pintar and Levec [6–8], who used commercial supported Cu catalysts in the CWO of phenol, a superior activity and stability against leaching of the active phase was recently claimed by Hočevar *et al.* [9] using ceria-supported Cu catalysts. In particular, they improved the resistance to leaching of the CuCeO$_x$ system in the CWO of phenol (150 °C) employing a special sol–gel synthesis route [12].

Furthermore, even under severe reaction conditions (190 °C), MnZrCeO$_x$ and CuZrCeO$_x$ catalyst feature a stable activity in the CWO of acetic acid [21].

Although activity and stability have been generally regarded as the independent properties of CWO catalysts, it has been documented that leaching of the active phase affects the performance of heterogeneous Cu-based systems in the CWO of phenol [10,11,22,23]. That is because leached out Cu ions enable a parallel *homogeneous reaction path* which markedly improves the intrinsic efficiency of the solid catalyst [9–11,22]. Nevertheless, Santos *et al.* [24,25] found that in bicarbonate-buffered reaction solutions (pH≈8) an alumina-supported Cu catalyst hinders the toxicity of phenol-containing streams, keeping also an excellent stability against leaching.

Therefore, this study illustrates a series of catalytic data in a wide range of experimental conditions which provide basic relationships amongst pH, Cu leaching

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and activity, aimed at highlighting the singular catalytic pattern of heterogeneous Cu-based systems in the CWO of phenol.

2. Experimental

CuCeO$_x$ catalyst was prepared by co-precipitation under controlled pH (≤5.5) conditions of $Cu(NO_3)_2$ and $(NH_4)_2Ce(NO_3)_6$ oxide precursors [9,22]. After precipitation, the catalyst was filtered, washed, dried at 100 °C (16 h) and further calcined at 500 °C (6 h). The Cu loading was then evaluated by AAS measurements, obtaining a result of 3.6 wt.%. An aliquot of the calcined sample was pre-treated in a H_2 flow at 300 °C (1 h) to attain a full reduction of the active phase [22].

Catalyst testing in the CWO of phenol in the range 130–170 °C was performed in a semi-batch mode, using a 0.25 L PTF-lined autoclave equipped with a magnetically driven turbine impeller (≈1000 rpm), keeping constant P_{O2} (7 atm) by continuous feeding at the rate of 200 stp mL min^{-1}. The initial phenol concentration (C_0) was fixed at 1000 ± 50 ppm (1 g L^{-1}) varying the catalyst load between 1 and 3 in terms of catalyst-to-phenol mass ratio (R). Liquid samples were periodically withdrawn from the reactor and analysed with respect to pH and phenol (HPLC), TOC and Cu^{2+} (AAS) concentration [22].

Temperature Programmed Reduction (*TPR*) measurements of the untreated catalyst (ca. 30 mg) in the range 20–800 °C were performed in a flow apparatus using a linear quartz micro-reactor (i.d., 4 mm), fed with a 6% H_2/Ar mixture flowing at 60 stp mL min^{-1}, and heated at the rate of 12 °C min^{-1} [22]. The hydrogen consumption was monitored by a TCD connected to a PC for data storage and processing after quantitative calibration of peaks area by known amounts of CuO [22]. TPR analyses were carried out after *in situ* steady-state (30 min) or pulse (0.2 stp mL) reduction treatment of a catalyst sample by hydrogen in the gas-phase at 160 °C and subsequent reoxidation by cyclic injection of oxygen pulses (0.2 stp mL) at the same temperature.

3. Results and discussion

3.1. Catalytic pattern

Experimental activity data in the CWO of phenol of the CuCeO$_x$ catalyst in the range 130–170 °C are shown in figure 1 in terms of phenol and TOC conversion (a) and pH and concentration of leached out Cu ions (b) against reaction time. A rise of reaction temperature

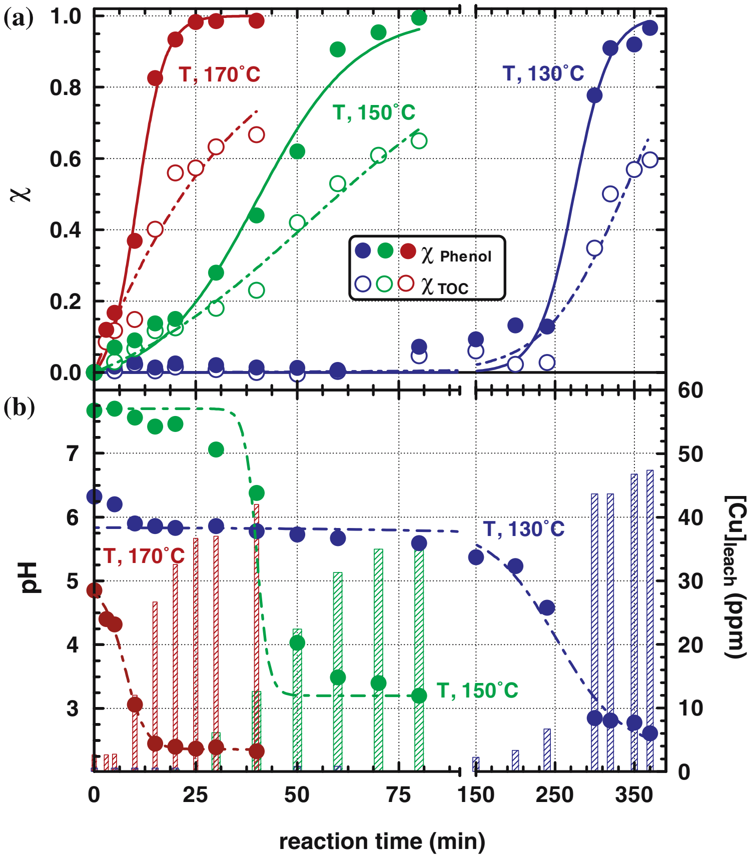

Figure 1. Effect of the reaction temperature on the CWO of phenol on CuCeO$_x$ catalyst (P_{O2}, 7 atm; R, 1). (a) Phenol and TOC conversion vs. reaction time; (b) pH and $[Cu]_{leach}$ vs. reaction time.

enables a regular increase of the CWO activity evidenced by a shortening of time required for a complete (90–100%) conversion of the substrate from ca. 6 h (130 °C) to 0.5 h (170 °C), respectively. The mineralization efficiency, directly related to the TOC decrease, attains a final value of ca. 60% at any temperature, concomitantly with the full substrate conversion (figure 1a). Moreover, irrespective of temperature, both phenol and TOC conversion depict peculiar 'S-shaped' trends, diagnostic of kinetic regimes varying with the extent of conversion [6–9]. As a rule, after an 'induction time' inversely correlated to the temperature, a fast kinetic regime leads to a sharp rise of phenol and TOC conversion. Meanwhile, the pH of the reacting solution (figure 1b) falls abruptly from initial neutral values (6–7) into acidic range, tending smoothly to final values of ca. 2–3. This trend, closely mirroring the conversion curves (figure 1a), reflects the formation of light acidic intermediates (e.g., oxalic, formic, acetic acid etc.) refractory to final mineralization under the adopted conditions [1,2,6–12,22–25]. Then, the pH decrease enables a simultaneous dissolution of Cu from the catalytic system (figure 1b) speeding up, in turn, the reaction kinetics by the establishment of a parallel homogeneous reaction channel [6,10,11,22]. This is documented by simultaneous variations of the derivative curves shown in figure 2a, which monitor the changes in reaction and leaching rate with time. Actually, these findings entail a close relationship amongst chemical composition of the reacting medium, rate of Cu leaching and reaction kinetics [6–11,22–25], as evidenced by exponential-like relationships between derivative conversion of phenol and TOC and the rate of Cu leaching shown in figure 2b. Anyway, final $[Cu]_{leach}$ values of 35–45 ppm (figure 1b) signal a quasi-quantitative loss of the active phase at the end of any runs [22].

The above activity data were then analysed according to the autocatalytic kinetic model [6,9] in order to obtain kinetic constants of phenol and TOC conversion at different *T* (table 1) and verify the consistency of apparent activation energy data [6–8,10,26]. Accounting for the effect of temperature, such figures result in reliable straight-line Arrhenius plots (figure 3), corresponding to apparent activation energy values equal to 88(±8) and 94(±9) kJ/mol for phenol and TOC conversion, respectively. Noteworthy, these values are in a

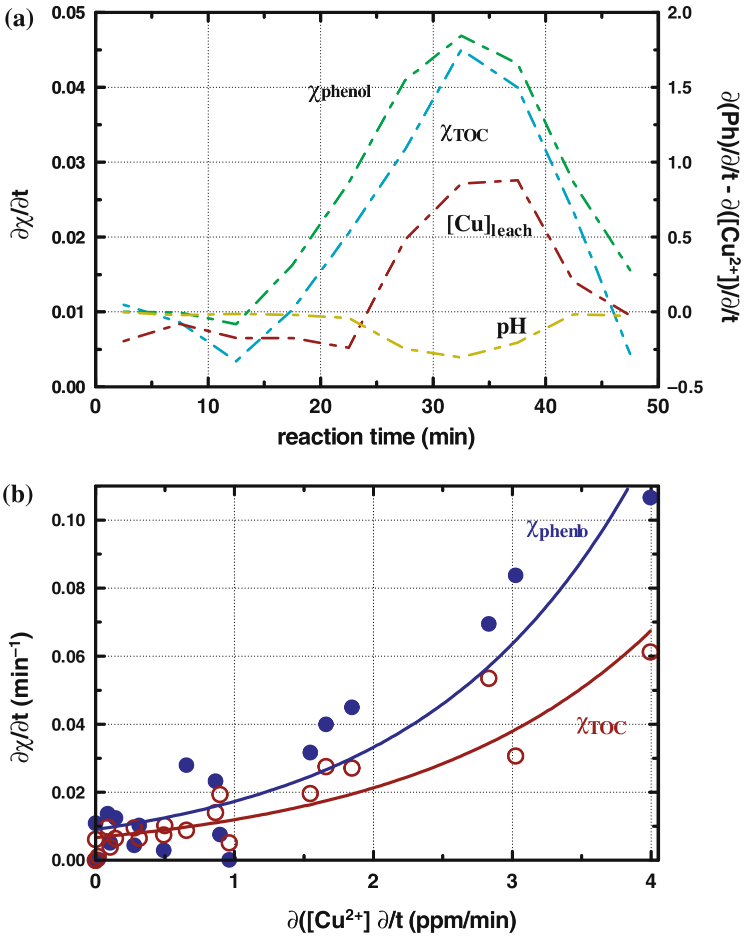

Figure 2. CWO of phenol on CuCeO$_x$ catalyst (*T*, 150 °C; P_{O2}, 7 atm; *R*, 1). (a) Rates of phenol and TOC conversion, of pH variations and Cu leaching vs. reaction time. (b) Rates of phenol and TOC conversion vs. rate of Cu leaching.

Table 1
CWO of phenol (R, 1). Values of the kinetic constants of phenol and TOC conversion according to the homogeneous autocatalytic reaction mechanism (refs. [6,9])

T (°C)	P (atm)	k_{phenol} (L s^{-1} mol^{-1})	k_{TOC} (L s^{-1} mol^{-1})
130	10	0.258	0.15
150	12	1.055	0.71
170	15	2.730	1.93

good agreement with literature data on the CWO of phenol by Cu catalysts [6–8,10,26], pointing thus to the occurrence of a common heterogeneous–homogeneous reaction path. Therefore, experimental results suggest that peculiar reaction kinetics and relative *induction time* find their explanation in the slow dissolution of Cu ions, driving an effective generation of hydroperoxy radicals by a homogeneous reaction mechanism, perhaps mediated by the Cu^{2+}/Cu^{+} redox couple [6,10,22].

The effects of the reaction pressure (a), catalyst-to-phenol mass ratio (b) and catalyst reduction (c), shown in figure 4, further confirm the peculiar behaviour pattern of Cu catalysts in the CWO of phenol (T, 150 °C). The negligible influence of the oxygen partial pressure on the rate of phenol and TOC conversion (figure 4a) essentially denotes the lack of relevant interphase resistances [6–8]. Moreover, according to a (*quasi*) zeroth-order dependence on oxygen concentration, it rules out the generation of active oxygen species as r.d.s., irrespective of the occurrence of heterogeneous or homogeneous reaction paths [1,6–8]. Also in this case the establishing of a fast kinetic regime parallels the sudden rise in $[Cu]_{leach}$, proving that the 'limiting step' lies in the dissolution of the active phase [22]. In fact, data in figure 4b shows that the rate of phenol and TOC conversion could not be even related to the catalyst-to-substrate mass ratio (R), as the reaction rate is slightly faster for a R value of 1 and keeps practically unchanged for R equal to 2–3 (figure 4b). Pointing to a minor role of the solid catalyst, the 'S-shaped' trend of the conversion curves mirror again simultaneous variations in pH and $[Cu]_{leach}$, still confirming the prevalent contribution of the homogeneous reaction path.

Also the chemical state of the active phase does not affect the aforesaid CWO pattern, the pre-reduced (300 °C) system featuring conversion values, variations in pH and resistance to leaching comparable with those of the calcined catalyst (figure 5). In this case it is, however, observable a shorter induction time due to an easier dissolution of the active phase from Cu/CuO particles in comparison to the leaching of Cu^{2+} ions strongly interacting with the support in the calcined system (see *infra*) [22].

At last, the influence of pH on the CWO performance of the studied system is displayed in figure 6. Although the rate of phenol conversion in a bicarbonate buffered (pH≈8) solution is comparable with that at 'free' pH conditions, the lack of an 'induction time' denote some remarkable changes in the main reaction path(s) [11,23–25]. In this case, phenol conversion increases

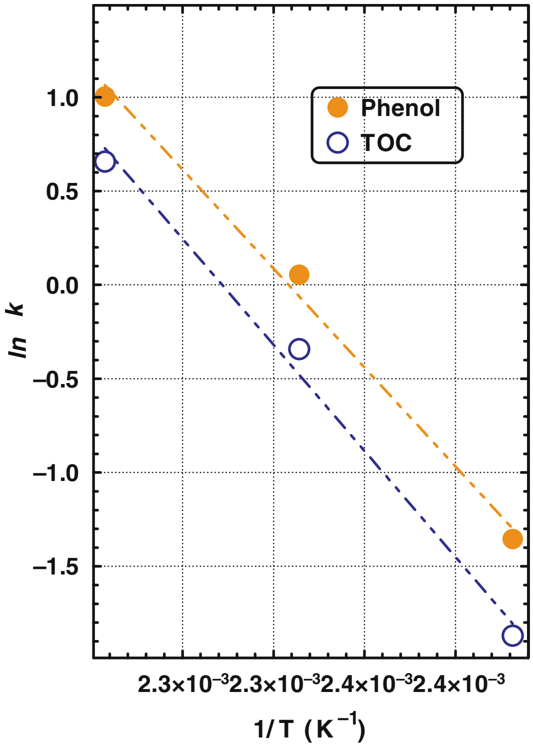

Figure 3. CWO of phenol on $CuCeO_x$ catalyst (P_{O2}, 7 atm; R, 1). Arrhenius plot of the kinetic constants of phenol and TOC conversion obtained from the autocatalytic kinetic model equation (see refs. [6,9]).

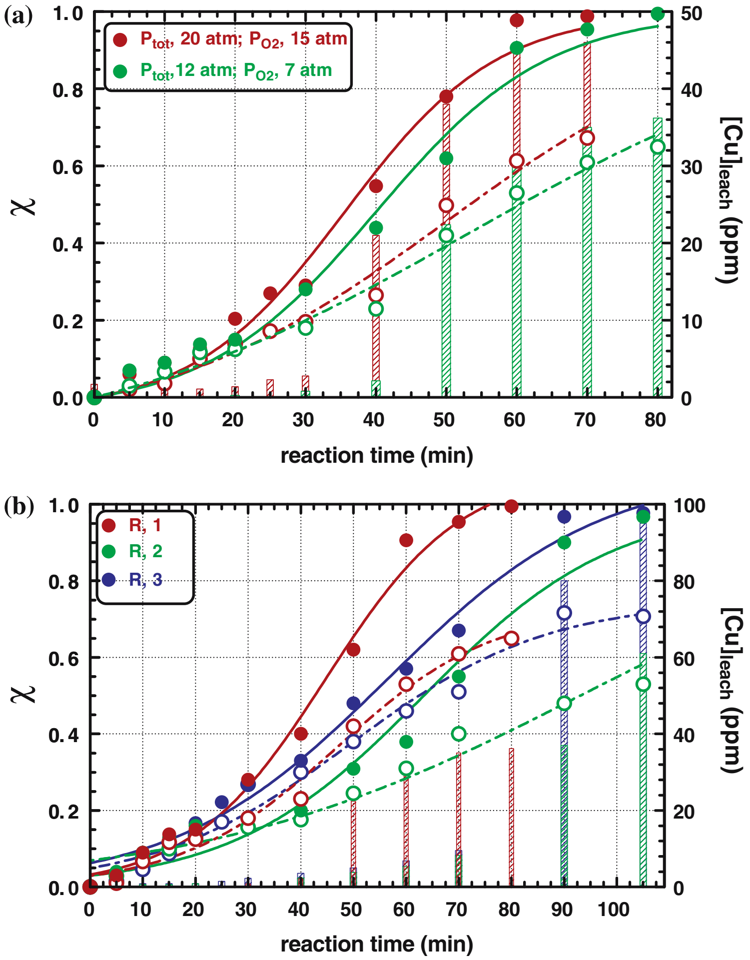

Figure 4. CWO of phenol on CuCeO$_x$ catalyst (T, 150°C; P_{O2}, 7 atm; R, 1). Influence of pressure (a) and catalyst-to-phenol mass ratio (b) on phenol and TOC conversion and $[Cu]_{leach}$.

sharply to ca. 60% during the first 10 min, thereafter rising smoothly to ca. 85% during 80 min; likewise the TOC conversion rises progressively to ca. 30% during the first 40 min keeping unchanged until the end of the run. Although a halved efficiency in phenol and TOC conversion with respect to those at 'free' pH conditions, no leaching of the active phase ($[Cu]_{leach}$ <1 ppm) could be detected under such conditions (figure 6). According

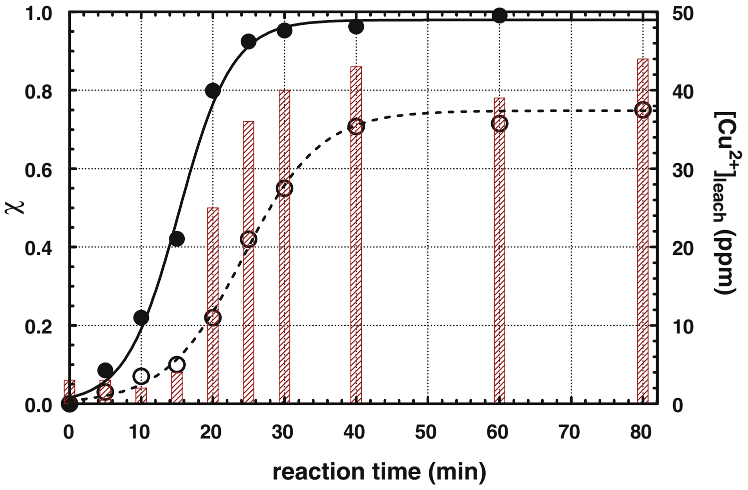

Figure 5. CWO of phenol on the pre-reduced (300 °C) CuCeO$_x$ catalyst (T, 150 °C; P, 12 atm; R, 1). Phenol and TOC conversion and $[Cu]_{leach}$ vs. reaction time.

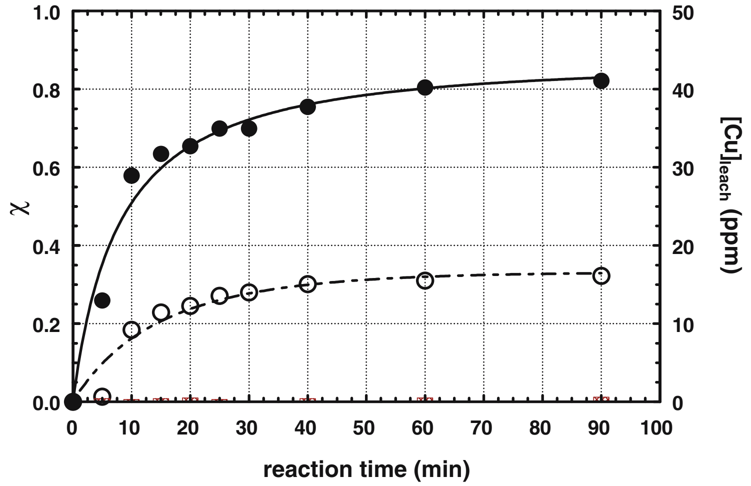

Figure 6. CWO of phenol on CuCeO$_x$ catalyst (*T*, 150 °C; *P*, 12 atm; *R*, 1) in a bicarbonate-buffered (pH≈8) reacting solution. Phenol and TOC conversion and [Cu]$_{leach}$ vs. reaction time.

to Santos *et al.* [23–25], these data entail a reaction mechanism driven by the catalyst surface, generating phenoxy radicals which subsequently react with bicarbonate ions, acting as a radical scavenger. Inhibiting the formation of the hydroperoxide radical species, which implies a lower mineralization efficiency, the formation of much lower toxic intermediates would be thus the most valuable achievement of Cu-based catalysts in bicarbonate-buffered streams [23–25].

3.2. Redox behaviour and catalytic mechanism

In order to ascertain the suitability of the CuCeO$_x$ system in driving a redox cycle under CWO conditions,

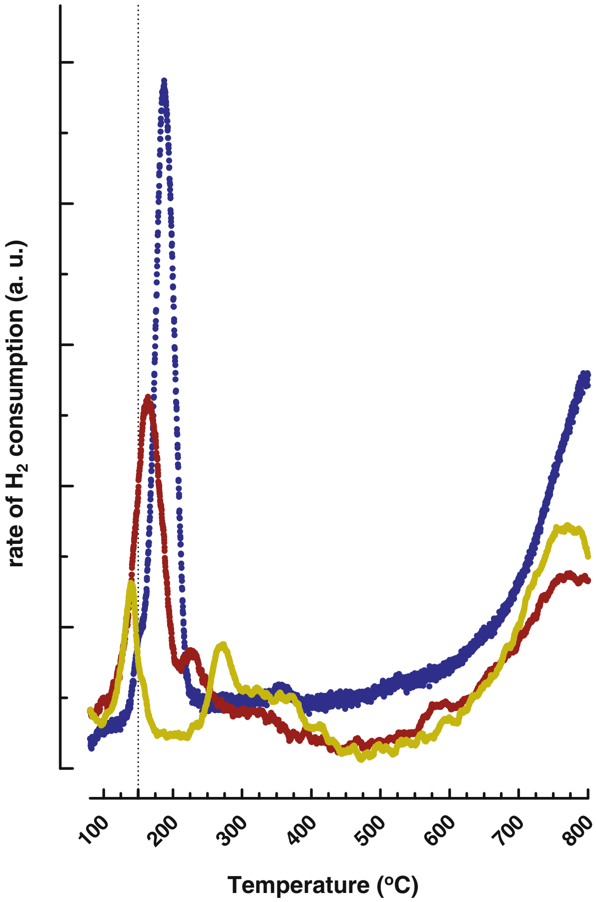

Figure 7. TPR profiles of the ‘as-prepared’ and gas-phase ‘reduced-oxidized’ (*T*, 160 °C) CuCeO$_x$ catalyst.

comparative TPR analysis of the catalyst, 'as-prepared' and subjected to gas-phase reduction/oxidation treatment have been performed. TPR spectra are compared in figure 7, while the values of reduction maxima and extents of H_2 consumption, referred to the reduction of Cu^{2+} (LT) and Ce^{4+} (HT) ions [22], respectively, are summarized in table 2. The TPR profile of the 'as-prepared' system displays a main reduction peak centred at 180 °C monitoring the reduction of highly dispersed *isolated* Cu^{2+} *ions* in a strong interaction with the support [22]. A corresponding *supra*-stoichiometric H_2 consumption (H_2/Cu, 1.30) signals in fact the concomitant reduction of surface neighbouring Ce^{IV} ions, due to a high dispersion of the active phases across ceria lattice [22]. This enables easy 'electron-transfer' processes at the Cu^{2+}/support interface which promote synergistically the redox features of the system [22]. A baseline drift at $T > 500$ °C, shaping a broad unless resolved peak with maximum at 775 °C, signals also an ongoing reduction of the ceria matrix in the bulk [22].

Actually, catalytic oxidation would entail an incipient reduction of active site(s) for generation of active oxygen species (e.g., peroxy, hydroperoxy, etc.) by *electron-transfer* prompting a surface-assisted reaction path [1,2,6,7,27]. A preliminary (partial) reduction of the catalyst by the substrate generates activated oxygen species yielding, in turn, a cyclic re-oxidation according to the general scheme [27]:

$$\text{Substrate} + \text{Site}_{\text{ox}} \xrightarrow{e^-} \text{Intermediate}_{\text{ads}} + \text{Site}_{\text{red}} \qquad (1)$$

$$O_2 + \text{Site}_{\text{red}} \xrightarrow{e^-} O_2^-; O_2^{2-}; O^- + \text{Site}_{\text{ox}} \qquad (2)$$

On account of this, it is likely that Cu^{2+} ions of the heterogeneous system could undergo the reduction by the substrate generating electrophilic, strongly oxidising, oxygen species, essential for an effective degradation of the C–C bond [1,2,6–8,11,22,27]. The incipient formation of light acidic intermediates enables in turn the dissolution of Cu^{2+} ions from the catalyst which enhances the reaction rate leading to the ultimate loss of the active phase [22]. Hindering any copper leaching in bicarbonate-buffered solutions, basic pH values drive a prevailingly heterogeneous reaction path [23–25]. However, both the deprotonation equilibrium of the substrate [24] and presence of huge amounts of HCO_3^- ions can concur to deeply affect the CWO mechanism. Even in the case of the pre-reduced catalyst (figure 5), a preliminary oxidation/dissolution of surface Cu^0 sites does not alter the fundamental features of the above reaction mechanisms.

Table 2

TPR data of the CuCeO$_x$ catalyst 'as-prepared' and reduced-oxidized at 160 °C

Catalyst	T_{M1} (°C)	T_{M2} (°C)	T_{M3} (°C)	H_2 consumption	
				(LT) H_2/Cu	(HT) H_2/Ce
'As-prepared'	180	–	775	1.30	0.14
'Reduced-oxidized'[a]	163	225	775	1.07	0.09
'Reduced-oxidized'[b]	140	273	768	0.31	0.09

[a] Reduced and oxidized at 160 °C under continuous O_2 flow for 30 min.

[b] Reduced and oxidized at 160 °C by O_2-pulses injection.

Therefore, irrespective of experimental conditions, catalyst formulation and treatments, general relationships among pH, rate of Cu leaching and phenol conversion can be depicted, as shown in figure 8. Namely,

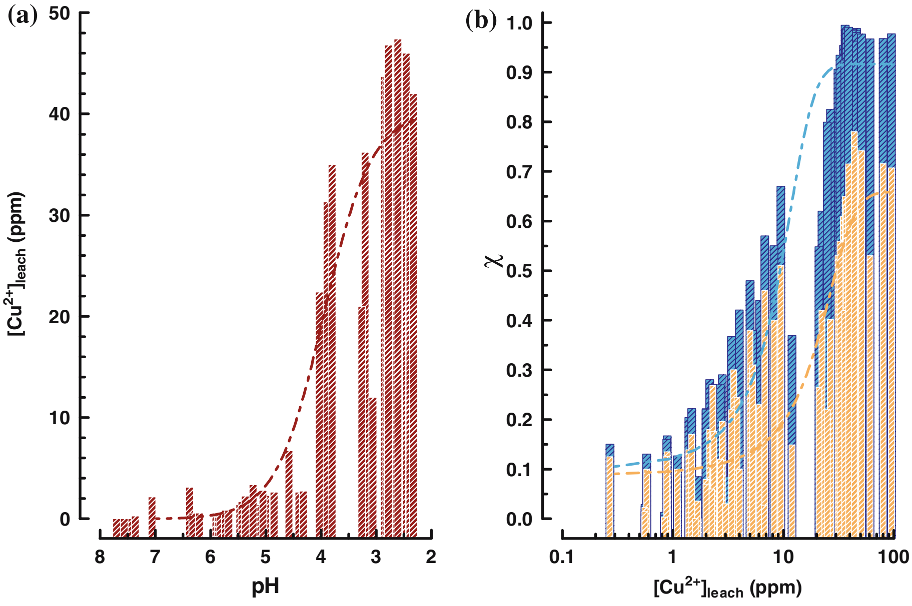

Figure 8. Summary of CWO activity data under 'free' pH conditions: (a) $[Cu]_{leach}$ vs. pH and (b) phenol and TOC conversion vs. $[Cu]_{leach}$.

figure 8a indicates in a window of pH comprised between 4.5 and 4.0 the critical value for an effective dissolution of the active phase, prompting the homogeneous catalytic reaction path. This implies a marked enhancement of kinetics of phenol and TOC conversion (figure 8b), confirming the peculiar CWO mechanism of Cu-based systems under 'free' pH conditions [6–8,10,11,22–26].

Furthermore, showing a considerable decrease of the active phase peak area, the TPR profiles of the catalyst subjected to gas-phase reduction/oxidation treatment at 160 °C (figure 7) indicate that the active phase cannot undergo a fully reversible redox cycle under reaction conditions (table 2). As the straight reduction of Cu^{2+} ions to metal Cu [22], a completely reversible redox cycle would be in fact hindered by the formation of 'nascent' metal clusters which modify irreversibly structure, morphology and solid-state interactions of the catalytic system. Then, the $CuCeO_x$ system likely undergoes the reduction step under reaction conditions (reaction 1) without restoring, however, the initial state (reaction 2) essential for a full reversibility of the surface-assisted reaction redox cycle. Therefore, these data signal that under 'free' pH conditions the stability of Cu-based catalysts could be seriously perturbed even in the absence of leaching phenomena of the active phase [23–25].

4. Conclusions

The catalytic pattern of ceria-supported copper catalysts in the CWO of phenol in a wide range of experimental conditions has been probed.

Regardless of catalyst composition and treatments, fundamental relationships amongst pH, extent of leaching and CWO activity have been outlined.

A parallel homogeneous reaction path by leached Cu ions markedly enhances the CWO activity of the solid catalyst under 'free' pH conditions, whereas a less effective fully heterogeneous path prevails in basic-buffered solutions.

A poor efficiency of the $CuCeO_x$ system in driving a fully reversible redox cycle under typical CWO conditions has been pointed out.

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