Reexamining the Formation of Environmentally Persistent Free Radicals from Aromatic Molecules on Metal Oxides

Franca Morazzoni¹

Received: 23 July 2021 / Accepted: 8 October 2021 / Published online: 15 October 2021
 © The Author(s) 2021

Abstract

The subject is a debate on the formation mechanism of the environmentally persistent free radicals (EPFR), by interaction of aromatics with transition metal oxides. Literature reports contrasting opinions concerning the stabilization of the phenoxyradicals mainly as concerns the suggested reduction of interacting transition metal centers. The present paper, in accordance with the mechanisms assessed by a number of spectroscopic and computational results, excludes the necessity that the catalytic mechanism involves the reduction of the metal centers by interaction with the aromatics.

Graphic Abstract

Keywords Environmentally persistent free radicals (EPFR) · Catalytic mechanism of formation

Combustion and thermal processes produce severe toxic components, like particulate matter, polychlorinated dibenzo-p-dioxins, polycyclic and aromatic hydrocarbons,

environmentally persistent free radicals (EPFR). These radicals are thought to be generated by interaction of aromatic compounds with the environmental transition metal oxides (iron, copper, zinc, nickel oxides) [1, 2] and are expected to produce reactive oxygen species (ROS) like $\text{OH}^\bullet$, $\text{O}_2^{\bullet-}$, $\text{HO}_2^\bullet$, $\text{HO}_2^{\bullet-}$, H_2O_2 [3]. ROS are able to induce biological damages, going from inflammation to serious DNA damage,

✉ Franca Morazzoni
 franca.morazzoni@unimib.it

¹ Department of Materials Science, University of Milano Bicocca, Via Cozzi 55, 20125 Milan, Italy

$\text{Al}_2\text{O}_3 > \text{ZnO} > \text{CuO} > \text{NiO}$ [6], in particular the radicals are most stable on ZnO. This is a highly ubiquitous oxide where the radical longevity may present an ongoing environmental hazard. Zn^{2+} centers cannot be significantly reduced to Zn^+ under contact by aromatics, thus the Dellinger's mechanism becomes even more questionable in this case. Very recently an investigation of the electronic state of ZnO after chemisorption of the aromatic molecule demonstrated, through photoelectron spectroscopy (XPS) and DFT calculations, that an electron transfer is active from the oxide to the aromatic molecules [7], opposed to that proposed by Dellinger. Accordingly the trend of the oxides in promoting the EPFR formation is parallel to their ability to stabilize the superoxide anion.

By collecting all these suggestions and mainly following the Cosentino mechanism [5], it seems to me that like in the case of CuO, a trigger action was played by O_2 also for ZnO. It is well known that the superoxide species $\text{Zn}^{2+}\text{-O}_2^-$ stabilizes at the oxide surface [8] Thus $\text{Zn}^{2+}\text{-O}_2^-$ can be thought the product of the electron transfer from ZnO to O_2 (probably via conduction electrons) and should allow the formation of the phenoxy radical on ZnO as well as on CuO, without reduction of Zn^{2+} (A_4 and A_5 in Scheme 1b).

A similar mechanism was reported by Orlandi, Morazzoni et al. [9] and is concerning the catalytic formation of the phenoxy radical by interaction between E-methyl ferulate (ROH) and [N,N'-bis(salicylidene)ethane-1,2-diaminato] cobalt(II), [Co(salen)]. The ESR investigation demonstrated the following pathway.

where the O_2 interaction allows the formation of the superoxide derivative $[\text{Co}(\text{salen})(\text{ROH})(\text{O}_2^-)]$ (step 1). The coordination of a second E-methyl ferulate, (step 2), removes O_2^- and gives rise to the phenoxy radical derivative. The above paper [9] also details that in the presence of a stronger electron donor molecule (like methanol or pyridine), the superoxide derivative remains stable and the phenoxy radical does not form.

It seems to us that the role of Zn^{2+} can be thought as parallel to that of Cobalt(II) in the organometallic process, that is the formation of the phenoxy radical on ZnO goes through that of a superoxide species. If this has high stability, the formation of the phenoxy radical is hindered. In

agreement with this opinion, the recent results reported by D'Arienzo et al. [10] outline that the phenoxy radical becomes stable on ZnO when the superoxide anion does not form. If, like in the case of defective ZnO, reactive oxygen vacancies are present and stabilize $\text{Zn}^{2+}\text{-O}_2^-$, the formation of the phenoxy radical is strongly inhibited.

The way of avoiding the formation of phenoxy radicals is to not diffuse oxide particles with regular surfaces.

Funding Open access funding provided by Università degli Studi di Milano - Bicocca within the CRUI-CARE Agreement.

Declarations

Conflict of interest The author has no conflict of interest for the present paper.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

1. Lomnicki S, Truong H, Vejerano E, Dellinger B (2008) Copper oxide—based model of persistent free radical formation on combustion-derived particulate matter. *Environ Sci Technol* 42:4982–4988
2. Kelley M, Hebert VH, Thibaux TM, Orchard MA, Hasan F, Cormier SA, Thevenot TP, Lomnicki SM, Varner KJ, Dellinger B (2013) Model combustion-generated particulate matter containing persistent free radicals redox cycle to produce reactive oxygen species. *Chem Res Toxicol* 26:1862–1871
3. Khachatryan L, Vejerano E, Lomnicki S, Dellinger B (2011) Environmentally persistent free radicals (EPFRs). 1. generation of reactive oxygen species in solution. *Environ Sci Technol* 45:8559–8566
4. Truong H, Lomnicki S, Dellinger B (2010) Potential for misidentification of environmentally persistent free radicals as molecular pollutants. *Environ Sci Technol* 44:1933–1939
5. D'Arienzo M, Gamba L, Morazzoni F, Cosentino U, Greco C, Lasagni M, Pitea D, Moro G, Cepek C, Butera V, Sicilia E, Russo N, Munoz-Garcia AB, Pavone M (2018) Experimental and theoretical investigation on the catalytic generation of environmentally persistent free radical from benzene. *J Phys Chem C* 121:9381–9393
6. Yang L, Liu G, Zheng M, Jin R, Zhao Y, Wu X, Xu Y (2017) Pivotal role of metal oxides in the formation of environmentally persistent free radicals. *Environ Sci Technol* 51:12329–12336

7. Petterson MC, DiTusa MF, McFerrin CA, Kurtz RI, Hall RW, Poliakov ED, Sprunger PT (2017) Formation of environmentally persistent free radicals (EPFRs) on ZnO at room temperature: implications for the fundamental model of EPFR generation. *Chem Phys Lett* 670:5–10
8. Morazzoni F, Scotti R, Minnaja N (1991) Reactivity of the surface paramagnetic species on polycrystalline ZnO and ZnO-supported ruthenium with hydrogen and carbon monoxide: an electron paramagnetic resonance investigation. *J Chem Soc Faraday Trans* 87:493–496
9. Bolzacchini E, Canevali C, Morazzoni F, Orlandi M, Rindone B (1997) Spectromagnetic investigation of the active species in the oxidation of propenoidic phenols catalysed by [N, N'-bis(salicylidene)-ethane-1,2 diam inato]cobalt(II). *J Chem Soc Dalton Trans.* <https://doi.org/10.1039/a705188c>
10. D'Arienzo M, Mostoni S, Crapanzaro R, Cepek C, Di Credico B, Fasoli M, Polizzi S, Vedda A, Villa I, Scotti R (2019) Insight into the influence of ZnO defectivity on the catalytic generation of environmentally persistent free radicals in ZnO/SiO₂ systems. *J Phys Chem C* 123:21651–21661

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.