



Surface reactivity of hydroxyl radicals formed upon catalytic decomposition of H₂O₂ on ZrO₂



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ABSTRACT

In this work, the surface reactivity of hydroxyl radicals formed upon catalytic decomposition of H₂O₂ on ZrO₂ in the presence of Tris(hydroxymethyl) aminomethane was studied experimentally. Two sets of competition experiments were performed: the competition between H₂O₂ and Tris for the surface bound hydroxyl radical (HO•) and between O₂ and H₂O₂ for the hydroxymethyl radical (•CH₂OH) (precursor for formaldehyde). A 5-fold increase in initial concentration of Tris or H₂O₂ does not lead to a 5-fold increase in CH₂O formation (only by a factor of 2–3 in the studied concentration range). The O₂-dependent enhancement of the final production of CH₂O becomes weaker upon increasing the initial concentration of H₂O₂ from 0.5 mM to 5 mM. The final production of CH₂O becomes independent of the concentration of Tris when [Tris]₀ is above 100 mM, i.e., the surface is saturated with Tris at this concentration. Based on the experimental results, a site-specific mechanism of H₂O₂ decomposition on the surface of ZrO₂ was proposed. This model was used for numerical simulations of the dynamics of the reaction system. The kinetics was simulated using the kinetic simulation software Gepasi 3.0 and the results are in good agreement with the experimental observations.

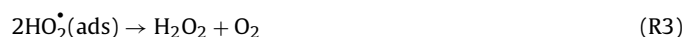
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1. Introduction

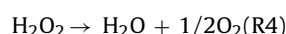
Radiation induced processes at solid–liquid interfaces are of significant importance for the operation and safety of most nuclear technological applications [1–4]. However, this is still a scarcely explored area. The main liquid phase in most systems of practical importance is water. The radiolysis products of water are e_{aq}[−], H•, HO•, H₂, H₃O⁺ and H₂O₂ [5]. As a stable molecular oxidizing product, the reactivity of H₂O₂ in both homogeneous and heterogeneous systems is intriguing and has been investigated in nuclear technology as well as in other fields such as catalysis, medical sciences and environmental chemistry [6–10]. Nevertheless, given the complexity of heterogeneous systems, the knowledge of the surface reactivity of H₂O₂ is still quite limited. The type of solid surface of importance in most systems of practical relevance is oxide (usually metal oxide) surface on metallic support, i.e., corroded metal surface. There are three types of oxides which are of primary significance in nuclear industry. These are UO₂ as matrix for most nuclear fuels, ZrO₂ formed on the surface of the fuel cladding and iron

oxides, since iron is the main constituent of most of the construction materials.

H₂O₂ can react with oxides via redox reactions as well as through catalytic decomposition [11,12]. It has been shown that both reactions occur if the metal is not in its highest oxidation state [7]. For instance, UO₂ has been studied intensively regarding both redox reactions and catalytic decomposition [7,13–15]. In contrast, only catalytic decomposition is observed when the oxide cannot be oxidized further [7,16,17]. Among such oxides, ZrO₂ is the most investigated one [16,18,19]. The mechanism of catalytic decomposition of H₂O₂ on the surface of oxides can be concluded from previous works [17,18] and is summarized as follows:



The overall reaction is



The produced intermediate radicals in (R1) and (R2) are bound to the oxide surfaces and for this reason, their half-lives may be prolonged significantly to several hours or even up to days [20,21]. It has been verified that the hydroxyl radical is the primary prod-

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uct in the catalytic decomposition of H_2O_2 by both experimental and theoretical means [16,18,22]. $\text{HO}^*(\text{ads})$ may react further on the interface, thereby affecting the whole system. The presence and reactivity of surface bound hydroxyl radicals, $\text{HO}^*(\text{ads})$ is of key significance in the study of catalytic decomposition of H_2O_2 . Nonetheless, the knowledge of such interfacial radical reactions is very limited. For instance, the amount of surface active sites is of utmost importance but is impossible to define so far.

It is well-known that Tris can react with the hydroxyl radical via hydrogen abstraction yielding formaldehyde which can be detected quantitatively by a modified version of the Hantzsch method [23,24]. Tris is a qualified probe to fulfill not only the basic requirements as a hydroxyl radical scavenger, but also by stabilizing the solution pH [16,18,25–27]. Therefore, Tris can be used to quantify the produced hydroxyl radicals indirectly by considering the yield of formaldehyde (proportional to the amount of scavenged radicals) upon reaction with hydroxyl radicals under specified condition [16,19]. The detailed mechanism of the reaction between the hydroxyl radical and Tris was reported in our recent work [19] which demonstrated that the yield of formaldehyde is greatly enhanced by the presence of O_2 and increase of pH in both homogeneous and heterogeneous systems. The integrated mechanism includes both pH- and O_2 -dependent pathways. The produced hydroxymethyl radical ($^*\text{CH}_2\text{OH}$) is the precursor of formaldehyde in the presence of O_2 [28]. In addition, H_2O_2 is able to compete with O_2 in reacting with $^*\text{CH}_2\text{OH}$ also forming formaldehyde [28,29].

The competition between H_2O_2 and Tris in reacting with the hydroxyl radical in homogeneous aqueous solution is also well-known, with rate constants of $2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively [30,31]. The competition between the corresponding surface reactions depends on the relative rates of the reactions. However, in this case, the rates are given by the corresponding rate constants and the surface coverage. The relative surface coverage is mainly determined by the solution concentrations and the relative affinity of the adsorbents to the oxide surface in case they adsorb to the same sites. It has been shown previously [26] that H_2O_2 has a significantly higher affinity toward TiO_2 than Tris does. In addition, H_2O_2 and Tris do not appear to compete for the same surface sites on TiO_2 [26].

In this study, we investigate the competition between H_2O_2 and Tris in the reaction with surface bound hydroxyl radicals formed upon catalytic decomposition of H_2O_2 on ZrO_2 . In addition, the effect of O_2 on the formaldehyde production at different $[\text{H}_2\text{O}_2]_0/[\text{Tris}]_0$ ratios is evaluated. On the basis of the experimental findings, an overall reaction mechanism and a kinetic model are derived. Numerical simulations using the kinetic model are in good agreement with experimental data.

2. Experimental

2.1. Instrumentation

The specific surface area of ZrO_2 was determined by using the Brunauer–Emmett–Teller method of isothermal adsorption and desorption of a gaseous mixture consisting of 30% N_2 , 70% He in a Micrometrics Flowsorb II 2300 instrument. The samples were weighed using a Mettler Toledo AT261 Delta Range microbalance. The experiments were performed in aqueous solution saturated by N_2 ($\geq 99.999\%$, Strömdøllen A/S) or saturated by air using Millipore water. The powder suspensions were stirred using a Heidolph MR3001K magnetic stirrer at 750 rpm. UV–vis spectra were collected by a Thermo Scientific Genesys 20 UV–vis spectrophotometer. The pH of solution was measured by Metrohm 713 pH meter with an accuracy of ± 0.1 pH units, calibrated by standard pH reagents.

2.2. Reagents and experiments

All the solutions used in this study were prepared using Milli-pore Milli-Q water.

Zirconium dioxide, ZrO_2 (CAS[1314-23-4], Aldrich 99%, $5 \mu\text{m}$), was baked at 500°C for 12 h before use in order to remove hydrocarbon contaminates. The powder pattern was indexed as monoclinic. The B.E.T. specific surface area is $5.0 \pm 0.2 \text{ m}^2 \text{ g}^{-1}$. The H_2O_2 solutions were prepared from a 30% standard solution (Merck). Produced hydroxyl radicals are scavenged by Tris(hydroxymethyl) aminomethane (CAS[77-86-1], BDH Chemicals, 99%). Acetoacetanilide AAA(CAS[102-01-2], Aldrich, $\geq 98\%$) and ammonium acetate (CAS[631-61-8], Aldrich, $\geq 98\%$) was used for quantifying formaldehyde with the modified version of the Hantzsch reaction [23,24]. As reported, the error of this method is $<2\%$ [16].

The reactions between H_2O_2 and ZrO_2 were performed at room temperature under different conditions to study the two competitions: H_2O_2 and O_2 in oxidizing $^*\text{CH}_2\text{OH}$ and H_2O_2 and Tris in reacting with surface bound HO^* .

The experiments were performed in parallel with N_2 -saturated (O_2 free) or air-saturated $\text{H}_2\text{O}_2/\text{ZrO}_2/\text{Tris}$ suspensions in sealed vials; magnetic stirring at a rate of 750 rpm was employed in both cases. Although the addition of hydroxyl radical scavenger will lower the yield of O_2 in H_2O_2 – ZrO_2 system, the influence in the present work is negligible as compared to significant amount of N_2/air [22]. The pH was adjusted to 7.5 by HCl/NaOH after mixing Tris and ZrO_2 . The powder surface area to solution volume ratio ($\text{SA}_{(\text{ZrO}_2)}/V$) was fixed at $4.5 \times 10^5 \text{ m}^{-1}$ which is in line with previous study [19]. $[\text{Tris}]_0$ varied from 20 mM to 400 mM and $[\text{H}_2\text{O}_2]_0$ varied from 0.5 mM to 5 mM. A sample was only taken when the reaction was completely finished (after 16 h). The sample ($\sim 2.0 \text{ mL}$) was extracted from the reaction vessel and then filtered through a $0.2 \mu\text{m}$ cellulose acetate syringe filter. The concentration of CH_2O was measured by the modified Hantzsch method [23,24].

The kinetic simulation software Gepasi 3 was utilized to build up the model for H_2O_2 decomposition on the surface of ZrO_2 in the presence of Tris. The software has been widely applied in kinetic simulation studies [32,33]. All the related kinetic parameters were adapted to the reported experimental ones [16,26].

3. Results and discussion

3.1. Experiments

A previous study performed under slightly different conditions showed that the final production of CH_2O is increased by 30% in air-saturated solutions compared to N_2 -saturated solutions at $[\text{Tris}]_0 = 20 \text{ mM}$ and $[\text{H}_2\text{O}_2]_0 = 5 \text{ mM}$ [19]. However, this observation is insufficient to fully evaluate the two cases of competing reactions: O_2 and H_2O_2 oxidizing $^*\text{CH}_2\text{OH}$ and H_2O_2 and Tris reacting with HO^* . Therefore, we varied $[\text{Tris}]_0$ (20, 100, 200, 400 mM) and $[\text{H}_2\text{O}_2]_0$ (0.5–5 mM), keeping all other parameters constant. The final production of CH_2O in different atmospheres (N_2 and air) and different Tris concentrations (20 and 100 mM) is plotted as a function of initial concentration of H_2O_2 (presented in Fig. 1).

It can clearly be seen from Fig. 1 that higher concentration of Tris leads to higher final concentration of formaldehyde ($[\text{CH}_2\text{O}]_f$) at a given initial H_2O_2 concentration ($[\text{H}_2\text{O}_2]_0$) both in the presence and absence of O_2 . Increasing the initial H_2O_2 concentration of a given Tris concentration also results in increased formaldehyde production. However, it is evident that a 5-fold increase in Tris or initial H_2O_2 concentration does not lead to a 5-fold increase in formaldehyde production (only by a factor of 2–3 in the studied concentration range). This apparent inconsistency can simply be attributed to the fact that formaldehyde is formed via a surface

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