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Confirming the Formation of Hydroxyl Radicals in the Catalytic Decomposition of H_2O_2 on Metal Oxides Using Coumarin as a Probe

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Hydrogen peroxide can be catalytically decomposed to O_2 and H_2O on metal oxide surfaces in contact with aqueous solutions containing H_2O_2. The initial step in this process has been proposed to be the formation of surface-bound hydroxyl radicals which has recently been verified using tris as a radical scavenger. Here, we make use of the unique fluorescent product 7-hydroxycoumarin formed in the reaction between hydroxyl radicals and coumarin to probe the formation of surface-bound hydroxyl radicals. The experiments clearly show that 7-hydroxycoumarin is formed upon catalytic decomposition of H_2O_2 in aqueous suspensions containing ZrO_2-particles and coumarin, thereby confirming the formation of surface-bound hydroxyl radicals in this process. The results are quantitatively compared to results on the same system using tris as a probe for hydroxyl radicals. The effects of the two probes on the system under study are compared and it is concluded that coumarin has a significantly lower impact on the system.

Highly reactive hydroxyl radicals can be produced in several different ways. One of the most straightforward ways is radiolysis of water where the absorption of ionizing radiation results in the formation of $^{\bullet}OH$, e_{aq}^{-}, $H^{\bullet}$, H_2O_2, H_2, $HO_2^{\bullet}$ and H_3O^+.[1] Heterogeneous photocatalysis using TiO_2 or other semiconducting materials as well as the homogeneous Fenton reaction are other possibilities.[2,3] It has been known for quite some time that metal oxides can catalyse the decomposition of H_2O_2 in aqueous solution producing O_2 and H_2O.[4] The mechanism for this process was proposed to proceed via the formation of hydroxyl radicals according to the following mechanism [Eqs. (1) to (3)]:[4]

$$H_2O_2 \rightarrow 2\ ^{\bullet}OH \tag{1}$$

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \tag{2}$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{3}$$

It is important to note that the hydroxyl radicals formed here are adsorbed to the catalyst surface (a prerequisite for this reaction to occur spontaneously) and therefore probably display a different reactivity from free hydroxyl radicals. The formation of hydroxyl radicals in catalytic decomposition of H_2O_2 on metal oxides was later confirmed using tris(hydroxymethyl)-aminomethane (tris) as a scavenger.[5] The nature of surface-bound hydroxyl radicals has been investigated fairly extensively using DFT.[6,7] Quite recently, the surface bound hydroxyl radical formed in the first step of the catalytic decomposition of H_2O_2 on oxide surfaces has also been found to play a major role in the oxidative dissolution of used UO_2-based nuclear fuel under waste repository conditions.[8] In general, catalytic decomposition of H_2O_2 on metal oxide surfaces is an important process in nuclear technology (to understand radiation induced corrosion) and it can also be used as an advanced oxidation technique (AOT) to purify water from organic pollutants.

One of the products formed upon the reaction between $^{\bullet}OH$ and tris is formaldehyde, which can be quantified fairly easily. This method was first used to detect hydroxyl radicals produced upon catalytic decomposition of H_2O_2 on ZrO_2.[5] Following the first study on ZrO_2, numerous experimental studies on other oxides have been performed.[6,9,10] In many studies, methanol has been used as a scavenger for the hydroxyl radical. Also, this reaction produces formaldehyde. Both tris and methanol have also been used to quantify hydroxyl radicals produced by heterogeneous photocatalysis.[10] Although very useful in assessing hydroxyl radical formation in heterogeneous systems, it should be kept in mind that the reaction with either tris or methanol yielding formaldehyde is not necessarily unique for hydroxyl radicals. In principle, any radical species capable of abstracting a hydrogen atom from tris or methanol will produce formaldehyde. Hence, truly unambiguous evidence for hydroxyl radical formation calls for alternative radical scavengers where the reaction with hydroxyl radicals yields a unique product that cannot be formed from other hydrogen-abstracting radicals. A promising candidate is coumarin that upon reaction with the hydroxyl radical yields a number of hydroxylated products of which one is strongly fluorescent.[11] The primary step of the reaction is addition of the hydroxyl radical to form a radical-adduct followed by oxidation of the adduct (by O_2) to form the hydroxylated products. The fluorescent product is 7-hydroxycoumarin. Coumarin has been used to quantify hydroxyl radicals in radiation chemistry as well as in heterogeneous photocatalysis.[11–17] However, it has to the best of our knowledge not been used in

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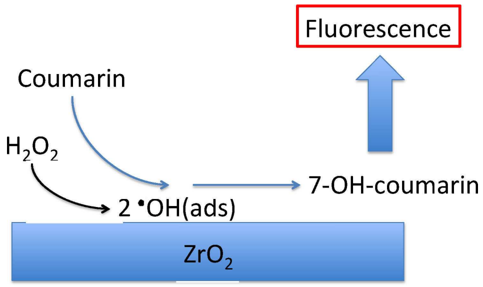
experiments monitoring the catalytic decomposition of H_2O_2 on metal oxide surfaces (Scheme 1).

In this work we have studied the possible formation of hydroxyl radicals in the reaction between H_2O_2 and ZrO_2 using coumarin as a probe. The experimental results are compared to the corresponding results using tris as a probe.

In heterogeneous photocatalysis, coumarin is sometimes claimed to scavenge hydroxyl radicals in the bulk rather than on the photocatalyst surface.[18] The bulk hydroxyl radicals are argued to be surface-bound hydroxyl radicals that have been desorbed and subsequently diffused away from the surface.[18] Given the strong adsorption of hydroxyl radicals to oxide surfaces demonstrated by both DFT calculations[6,7] and experiments assessing the reduction potential of the surface-bound hydroxyl radical compared to the free hydroxyl radical,[19] desorption of the radical would appear to be a very unlikely process. Also, the concentration dependence on the rate of coumarin hydroxylation in heterogeneous photocatalysis differs significantly from that observed in homogeneous gamma radiolysis (where hydroxyl radicals are produced homogeneously in solution) which points in the direction of surface-bound hydroxyl radicals in the case of heterogeneous photocatalysis.[12,20]

Although a high coumarin concentration (resulting in a larger amount of probe being adsorbed on the surface of the catalyst) would provide a higher radical scavenging capacity, the competing absorption of the excitation light by coumarin in the fluorescence measurement of 7-hydroxycoumarin drastically reduces the sensitivity of the method.[20] There are several ways to handle this problem. By far, the easiest way is to perform the calibration of the fluorescence measurements using solutions with the same coumarin concentrations as used in the experiments. If different coumarin concentrations are used, the samples can be diluted to the same coumarin concentration before the fluorescence measurement. Alternatively, calibrations can be performed at different coumarin concentrations.

The material of the reaction vessel as well as vigorous stirring or gas purging and frequent sampling turned out to affect the reproducibility of the experiments. In the end, the optimum conditions of the coumarin experiment were the ones described in the experimental section. Five parallel experiments were performed and the reproducibility turned out to be very high. The results from the two sets of experiments are presented in Figure 1.



Scheme 1. Principle for probing hydroxyl radical formation by using coumarin.

In both cases when ZrO_2 was present, H_2O_2 was completely consumed at the time of the sampling (24.5 h). The general trends in the two sets of experiments look very similar. A background signal (i.e., a signal in the absence of ZrO_2) is observed in both cases. The signal in the presence of ZrO_2 is significantly higher than the background after 24.5 h in both cases. The fact that 7-hydroxycoumarin is formed at levels significantly above the background in the system containing H_2O_2 and ZrO_2 serves as an independent confirmation that hydroxyl radicals are indeed formed in the catalytic decomposition of H_2O_2 on ZrO_2.

The relative yield of 7-hydroxycoumarin in the reaction between hydroxyl radicals and coumarin is known to be 5.7% from radiation chemical experiments.[12] In the same way, the formaldehyde yield for the reaction between the hydroxyl radical and tris has been determined to 35%.[5] By using the relative yields we can calculate the total concentration of scavenged hydroxyl radicals in the two systems.

For comparison we also calculate the fraction of trapped hydroxyl radicals per probe molecule (concentration of trapped hydroxyl radicals divided by total probe concentration) and the

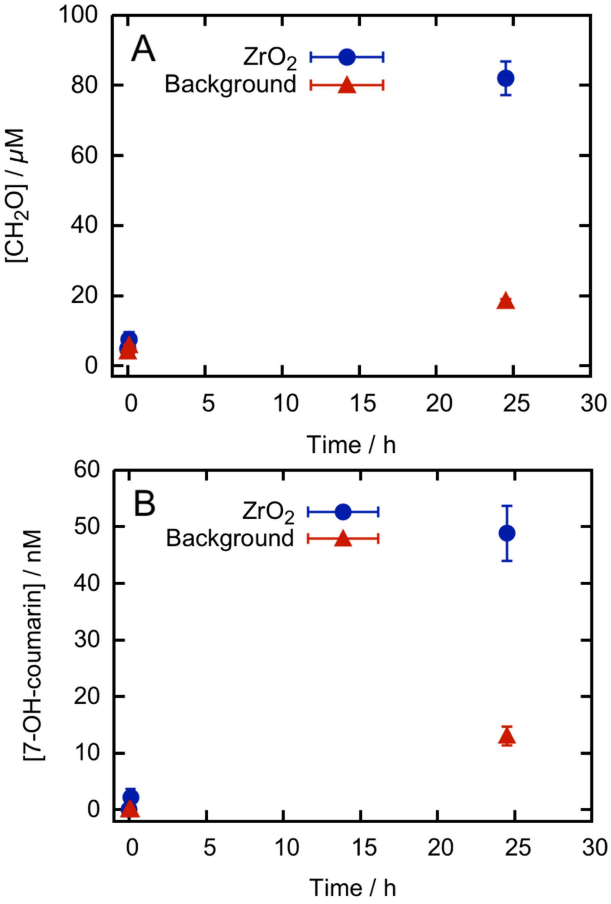


Figure 1. Concentration of formaldehyde (a) and 7-hydroxycoumarin (b) as a function of exposure time in experiments using tris (a) and coumarin (b) to scavenge hydroxyl radicals.

fraction of scavenged hydroxyl radicals per decayed H_2O_2. These results are summarized in Table 1.

The scavenging of surface-bound hydroxyl radicals is a surface reaction and its efficiency will depend on the amount of adsorbed radical scavenger. This situation is analogous to probing the efficiency of a heterogeneous photocatalyst. For heterogeneous photocatalysis, Langmuir-Hinshelwood kinetics can often be used to describe the probe concentration dependence.[21] Maximum scavenging capacity is reached when the photocatalyst surface is saturated with probe molecules. To reach this point, a sufficiently high concentration of the probe must be used. In a recent work on TiO_2-photocatalysis, the coumarin concentration dependence was explored and it was concluded that the solubility of coumarin is too low to get even close to surface saturation.[20] However, the affinity of coumarin towards the TiO_2-surface was assessed to be similar to that of tris.[20] Nevertheless, a fraction of the coumarin is adsorbed to the surface and capable of scavenging hydroxyl radicals. In a previous paper, the tris concentration dependence on the formaldehyde production rate in a system where H_2O_2 was catalytically decomposed on ZrO_2 was studied.[22] Interestingly, the concentration dependence paralleled the trend seen for TiO_2-photocatalysis (the rate of formaldehyde formation becomes independent of tris-concentration above 100 mM)[23] indicating that the affinity of tris towards ZrO_2 is similar to the affinity towards TiO_2. The difference in the amount of scavenged hydroxyl radicals between the tris and coumarin experiments in the present work is around a factor of 300 in favour of tris. Given the fact that the tris concentration is three orders of magnitude higher than the coumarin concentration and that the affinity of tris and coumarin towards oxide surfaces can be assumed to be similar, the observed difference in hydroxyl radical scavenging capacity between the two systems appears quite reasonable.

As can be seen in the table, the fraction of probe molecules consumed during the duration of the experiment is quite low in both cases. Only around 1 % of the coumarin is consumed while the consumption of tris corresponds to less than 0.4 %. In other words, the concentration of probe molecules can be considered constant throughout the experiment in both cases.

In general, the presence of a radical scavenger may influence the overall mechanism as well as the kinetics for catalytic decomposition of H_2O_2. The kinetics of H_2O_2 decomposition is affected unless reaction (1) is the rate limiting step. In a system containing a radical scavenger there are two competing reactions that consume the hydroxyl radical formed in reaction (1). The first reaction is hydrogen abstraction from H_2O_2, reaction (2), and the second is the reaction between the hydroxyl radical and the scavenger (probe). At high scavenger concentrations the yield of O_2 (reaction (3)) will be significantly reduced.[24] From Table 1 it can be seen that tris scavenges 0.09 hydroxyl radicals per decomposed H_2O_2. Theoretically, two hydroxyl radicals could be formed per decomposed H_2O_2 provided that the scavenger (tris) concentration is high enough to outcompete hydrogen abstraction from H_2O_2, i.e., H_2O_2 is only consumed in reaction (1). In a system without an added scavenger, the theoretical number of hydroxyl radicals formed per decomposed H_2O_2 is one (since H_2O_2 is consumed in the reaction with surface-bound hydroxyl radicals, reaction (2)). Hence, quantitative scavenging of hydroxyl radicals can only be achieved when the overall reaction system is severely altered by the presence of the probe. At the concentration used in this work, tris will have a small but significant effect on the reaction under study. Coumarin on the other hand only scavenges 3×10^{-4} hydroxyl radicals per decomposed H_2O_2. This is considered to be negligible. In this respect, a probe like coumarin can be seen as an alternative with minimal influence on the chemistry of the system since the sensitivity is quite reasonable also at low probe concentrations. However, under such conditions the probe only provides qualitative information.

Table 1. Summary of results from the hydroxyl radical scavenging experiments.

	Tris/CH_2O	Coumarin/7-hydroxycoumarin
Concentration of product due to reaction on ZrO_2	64 ± 5 μM	35 ± 5 nM
Concentration of scavenged hydroxyl radicals	180 ± 10 μM	620 ± 90 nM
Fraction of scavenged hydroxyl radicals per probe molecule	3.6×10^{-3}	1.2×10^{-2}
Fraction of scavenged hydroxyl radicals per decayed H_2O_2	0.09	3×10^{-4}

In this work we have confirmed the formation of hydroxyl radicals in the catalytic decomposition of H_2O_2 on ZrO_2 using coumarin as a selective probe. Apart from yielding a unique product upon reaction with hydroxyl radicals, coumarin is also demonstrated to be a sensitive probe capable of detecting hydroxyl radicals at probe concentrations low enough not to alter the overall surface chemistry.

Experimental Section

Two sets of experiments were performed using either coumarin or tris as radical scavengers. Purified water (18.2 MΩ.cm, Merck MilliQ) was used throughout and chemicals were of reagent grade or higher unless otherwise stated.

For experiments were coumarin was used as radical scavenger, 1.25 g ZrO_2 powder were suspended in aqueous coumarin solutions. H_2O_2 was added to the suspensions to reach a total volume of 50 ml, a coumarin concentration of 0.05 mM and a H_2O_2 concentration of 2 mM. In experiments were tris was used instead of coumarin, the pH of the tris solution was adjusted to 7.5 using HCl before adding ZrO_2. Afterwards, H_2O_2 was added to the powder suspensions to reach a total volume of 50 ml, a tris concentration of 50 mM and a H_2O_2 concentration of 2 mM. All powder suspensions (containing either tris or coumarin) where kept in polypropylene test tubes which were protected from light and constantly mixed using a test tube rocking mixer. Both sets of experiments were repeated 5 times to assure reproducibility. Background measurements with either coumarin or tris were also performed in sets of five but in the absence of ZrO_2. 2 ml aliquots were taken from the powder suspensions and the blank samples just before, 5 min as well as 24.5 h after the addition of H_2O_2. The aliquots were filtered through 0.2 μm cellulose acetate syringe filters to separate the powder from the solution. The concentrations of H_2O_2 as well as the products from the reaction between $HO^•$ and coumarin or tris were determined from the aliquots.

H_2O_2 concentrations were measured spectrophotometrically at 350 nm using the Ghormley triiodide method.[25]

Formaldehyde formed upon the reaction between tris and $HO^•$ can indirectly be measured by spectrophotometry at 368 nm using the modified Hantzsch method,[26,27] where a dihydropyridine derivative forms when 1.5 ml formaldehyde containing sample is left to react for 15 min with ammonium acetate (2.5 ml, 4 M) and acetoacetanilide (1 ml, 0.2 M) at 40 °C.

Coumarin reacts with $HO^•$ to form fluorescent 7- hydroxycoumarin (among other hydroxylated species), which was measured using a fluorescence spectrophotometer. A calibration for aqueous solutions containing 7- hydroxycoumarin (various concentrations) and 0.05 mM coumarin was used for quantification. The excitation wavelength was set to 326 nm and the emission was measured at 456 nm using a Cary Eclipse Fluorescence Spectrophotometer.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Hydrogen peroxide · Catalytic decomposition · Metal oxide · Surface-bound hydroxyl radicals · Coumarin

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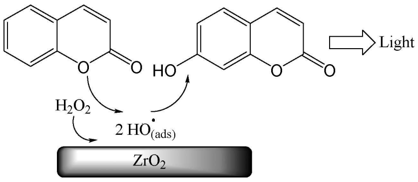
COMMUNICATIONS

New probes: By using fluorescence spectroscopy to quantify the formation of 7-hydroxycoumarin we confirmed the formation of hydroxyl radicals upon the catalytic decomposition of H_2O_2 on ZrO_2 in aqueous powder suspension.



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