



Disproportionation of hydrogen peroxide into singlet oxygen catalyzed by lanthanum-exchanged zeolites

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Abstract

Lanthanum(III) was immobilized on various zeolite supports by simple cation exchange. The resulting materials were tested in the disproportionation of H₂O₂ into singlet molecular oxygen (¹O₂). The rate of H₂O₂ disproportionation and the reaction of the formed ¹O₂ with citronellol as a typical olefinic substrate were strongly dependent on the zeolite topology and composition. Zeolites with a large crystal size, small pores, or a one-dimensional pore system showed low activity in the disproportionation of H₂O₂. In contrast, zeolites with a small crystal size or zeolites possessing large intersecting pores were active ¹O₂ generators. La supported on ultrastable Y zeolite (USY) and zeolite Beta were identified as the most active and efficient catalysts. Typically, within 24 h at 40 °C, 100 mol of citronellol hydroperoxides is produced per mol of La supported on USY zeolite. Within this time, 800 mol of H₂O₂ is disproportionated into ¹O₂. In comparison with unsupported La-hydroxide, La-USY shows a significantly higher activity and a slightly more efficient use of H₂O₂. The heterogeneous nature of the catalysis by La-USY was verified by filtration tests, and its stability was proved by X-ray diffraction and recycle experiments. Finally, the catalyst was used in the peroxidation of various olefinic compounds. Compared with conventional molybdate catalysts, La-USY is particularly useful for the selective peroxidation of allylic alcohol derivatives, with very little competitive epoxidation and no alcohol oxidation being observed.

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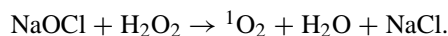
Keywords: Chemiluminescence spectroscopy; Heterogeneous catalysis; Hydrogen peroxide; Hydroperoxides; Lanthanum; Oxidation; Singlet oxygen; Zeolites

1. Introduction

Chemical production of singlet molecular oxygen, ¹O₂ (¹Δ_g), with the use of readily available reagents such as hydrogen peroxide, might provide a safe and inexpensive alternative to the currently used photochemical generation of singlet oxygen [1–3]. Although the latter method is still most frequently used in organic synthesis, it requires substantial investments in complicated gas/liquid photoreactors, which do not profit from an economy of scale. Moreover, large-

scale photooxidation entails hazardous processing conditions because of the combination of light, organics, and dioxygen. As a result, industrial photooxidation is limited to the manufacture of low-volume, high-value compounds such as aroma chemicals [4].

A frequently used chemical source of ¹O₂ is the oxidation of H₂O₂ by aqueous sodium hypochlorite [5–7]



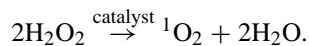
The reaction produces a stoichiometric amount of chloride salt, and the rate of reaction is not easily controlled. Therefore, a significant part of the formed ¹O₂ is lost in gas bub-

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bles. Moreover, hypochlorite can induce side reactions such as chlorination or epoxidation.

A milder method for the chemical production of $^1\text{O}_2$ is the metal-catalyzed disproportionation of H_2O_2 . Several inorganic compounds such as Na_2MoO_4 , Na_2WO_4 , and $\text{Ca}(\text{OH})_2$ are known to catalyze this reaction [8]



The key step is the formation of peroxo-metal intermediates, which disproportionate into singlet oxygen and water. The molybdate/ H_2O_2 system has proved to be useful for the peroxidation of olefinic compounds because of its high efficiency in generating $^1\text{O}_2$ under mild reaction conditions [2,9–13]. Moreover, highly active heterogeneous Mo catalysts have been prepared by the immobilization of molybdate on anionic clays [14–17]. However, a disadvantage of these Mo catalysts is their low selectivity in the $^1\text{O}_2$ oxidation of allylic alcohol and allylic amine derivatives [18]. The low selectivity is due to the enhanced tendency of allylic alcohols to undergo epoxidation via direct oxygen-atom transfer from peroxo-Mo species [19,20]. Moreover, in the oxidation of secondary allylic alcohols, enone formation might compete.

Recently, the use of lanthanum(III) and H_2O_2 for the selective $^1\text{O}_2$ oxidation of allylic alcohols to the corresponding hydroperoxy homoallylic alcohols was reported [18,21]. Moreover, it was found that $\text{La}/\text{H}_2\text{O}_2$ is able to peroxidize certain allylic amines, a reaction that cannot be carried out successfully with conventional Mo catalysts because of competing *N*-oxidation [22]. Disadvantages of La, however, are the lower activity and the less efficient use of H_2O_2 compared with Mo. These drawbacks may be related to the appearance of the active catalyst as a peroxidized La-oxo/hydroxo precipitate. This material is a solid possessing a dense gel structure, which may cause mass transfer limitations. The latter is important in view of the short lifetime of $^1\text{O}_2$. A typical value in water is 4.5 μs , corresponding to a mean travel distance of 200 nm [23]. In addition, the presence of numerous low-frequency O–H bonds in the La-hydroxide gel may induce enhanced quenching of $^1\text{O}_2$ [24,25]. Therefore, dispersion of lanthanum on a suitable support might enhance the activity of the catalyst by allowing higher diffusion rates. Moreover, a larger portion of the formed $^1\text{O}_2$ may react with the substrate instead of being lost by quenching.

Very recently we have shown that La-exchanged zeolites can be used as active and selective catalysts for the generation of $^1\text{O}_2$ from H_2O_2 [26]. Zeolites are suitable supports for this reaction because of their high surface area, rigid framework, high thermal and oxidative stability, and large cation exchange capacity. Moreover, La-exchanged zeolites are widely used in the petrochemical industry (e.g., catalytic cracking) [27–32], although their application in the synthesis of fine chemicals, especially in the field of oxidation chemistry, is rather unexplored [33,34].

In this study, various support materials were evaluated in the La-catalyzed generation of $^1\text{O}_2$ from H_2O_2 . Zeolites were compared with other support materials such as clays and ion-exchange resins and with unsupported La catalysts such as $\text{La}(\text{OH})_3$ and La_2O_3 . Next, the most promising catalyst, La-USY zeolite, was optimized, and the influence of reaction conditions on the activity and efficiency of this catalyst was studied. Finally, the scope of the La-USY catalyst was determined in the peroxidation of various olefinic compounds.

2. Experimental

2.1. Materials

All materials were obtained from commercial sources and were used without purification. Allylic alcohols were supplied by Mercachem. Hydrogen peroxide was a 50 wt% aqueous solution from Acros. Commercial 30 and 50 wt% H_2O_2 could be used interchangeably, providing similar results. H_2O_2 and alkyl hydroperoxide solutions are strongly oxidizing and should be handled with appropriate precautions.

Data on the origin and some physicochemical properties of the zeolite supports are compiled in Table 1. The properties of the USY zeolites used in this work have already been described in detail [35,36]. Montmorillonite (K10), Laponite, and Amberlyst 15 were obtained from Aldrich, Laporte Inorganics, and Janssen Chimica, respectively.

2.2. Synthesis and characterization of La catalysts

2.2.1. Preparation of La-exchanged zeolites

The catalysts were prepared by simple ion exchange of zeolites, cationic clays, or sulfonated resins with La^{3+} cations. For all catalyst preparations, distilled water was used.

Commercial H^+ zeolites or cationic clays were first converted to the NH_4^+ form by stirring for 1 h in aqueous NH_3

Table 1
Specifications and physicochemical properties of zeolites used in this work

Zeolite	Origin	Si/Al ^a	Size ^b (μm)	Surface area ^c (m^2/g)
Y	Zéocat	2.7	3.2	672
USY	PQ, CBV720	13.0	0.2–0.5	820
Beta	PQ, CP811BL-25	10.8	0.1–0.7	739
Mordenite	Norton, Zeolon 100	11.0	1.5–3.5	480
Dealuminated (deal.) mordenite	Zéocat, ZM510	6.5	1–2	530
A	Union Carbide	0.9	1–3	–
L	Uetikon, EXAR109	3	1	220
ZSM-5	Alsi-Penta, SN-27	13	–	–

^a Si/Al ratio from ^{27}Al NMR.

^b Crystal size as determined by SEM.

^c BET surface.

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