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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 H_2O_2 into singlet molecular oxygen ($^1O_2$). The rate of H_2O_2 disproportionation and the reaction of the formed $^1O_2$ 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 H_2O_2. In contrast, zeolites with a small crystal size or zeolites possessing large intersecting pores were active $^1O_2$ 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 H_2O_2 is disproportionated into $^1O_2$. In comparison with unsupported La-hydroxide, La-USY shows a significantly higher activity and a slightly more efficient use of H_2O_2. 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.

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

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1. Introduction

Chemical production of singlet molecular oxygen, $^1O_2$ ($^1\Delta_g$), 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 $^1O_2$ is the oxidation of H_2O_2 by aqueous sodium hypochlorite [5–7]

$$NaOCl + H_2O_2 \rightarrow {}^1O_2 + H_2O + NaCl.$$

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 $^1O_2$ 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 $^1O_2$ is the metal-catalyzed disproportionation of H_2O_2. Several inorganic compounds such as Na_2MoO_4, Na_2WO_4, and $Ca(OH)_2$ are known to catalyze this reaction [8]

$$2H_2O_2 \xrightarrow{\text{catalyst}} {}^1O_2 + 2H_2O.$$

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 $^1O_2$ 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 $^1O_2$ 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 $^1O_2$ oxidation of allylic alcohols to the corresponding hydroperoxy homoallylic alcohols was reported [18,21]. Moreover, it was found that La/H_2O_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 $^1O_2$. 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 $^1O_2$ [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 $^1O_2$ 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 $^1O_2$ 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 $^1O_2$ 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 $La(OH)_3$ 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.

(pH 10) at room temperature (1 g zeolite per 50 ml water). This procedure was repeated once. Next the NH_4^+ zeolites were converted to Na^+ zeolites by three successive ion exchanges with $NaNO_3$ for 24 h at room temperature (1 g zeolite per 50 ml of 0.5 M $NaNO_3$ in water). Between steps the zeolites were separated by filtration, washed with distilled water, and dried at 40 °C.

Commercial Na^+ zeolites were stirred only once in aqueous NH_3 and were ion-exchanged twice with $NaNO_3$ before La^{3+} exchange.

La zeolites containing 0.2 mmol La per gram of solid were prepared by ion exchange of Na^+ zeolites with $La(NO_3)_3 \cdot 6H_2O$ (1 g zeolite/50 ml water) for 24 h at 70 °C. The La zeolites were separated by filtration, washed with distilled water, and dried at 40 °C.

2.2.2. Physical measurements

The crystallinity and stability of the catalysts were evaluated by X-ray diffraction (XRD) with a Siemens D5000matic diffractometer and Ni-filtered Cu-K_α radiation of 0.1542 nm at 40 kV and 50 mA. Diffractograms were recorded between $2\theta = 4°$ and $2\theta = 55°$ with a scanning rate of 2θ 1°/min.

Infrared emission of $^1O_2$ was measured with a liquid nitrogen-cooled germanium photodetector (model EO-817L; North Coast Scientific Co., Santa Rosa, CA, USA) sensitive in the spectral region from 800 to 1800 nm with a detector of 0.25 cm^2 and a sapphire window. The detector was connected to a lock-in amplifier from Stanford Research Systems (model SR830 DSP) and was powered by a North Coast Scientific Corp. Bias Supply (model 823A).

2.3. Chemiluminescence experiments

2.3.1. Detection of the IR Luminescence of $^1O_2$ at 1270 nm

A typical chemiluminescence experiment was carried out as follows. A solution containing 2 g La zeolite (0.04 M La) and 550 µl NaOH (2 M) in 10 ml methanol was stirred at 35 °C, and the mixture was pumped continuously through a quartz cell placed in front of the germanium detector. Once the background noise of the IR signal was stable, 250 µl H_2O_2 (0.4 M, 50 wt%) was introduced. The intensity of the luminescence signal (I_p) was recorded as a function of time.

2.3.2. Determination of the $^1O_2$ yield by chemiluminescence measurements

For the determination of the $^1O_2$ yield produced by the La-zeolite/H_2O_2 systems, first a chemiluminescence signal was recorded in the absence of a chemical trap (Fig. 2). At the end of the reaction, a second batch of H_2O_2 was added to the reaction mixture. After stabilization of the IR signal, a known amount of α-terpinene was added to react with a part of the $^1O_2$ produced. This highly reactive chemical trap is known to react with $^1O_2$ by a pure chemical process. Hence, the missing area in the luminescence signal corresponds to the amount of $^1O_2$ trapped by α-terpinene. Since the total area under the curve is directly related to the cumulated amount of $^1O_2$ generated, comparison of the areas under the two curves recorded in the absence and presence of α-terpinene allows the determination of the total $^1O_2$ yield.

2.4. Catalytic experiments

2.4.1. Disproportionation of hydrogen peroxide

The composition of the reaction mixture was 10 ml alkaline methanol (0.02 M KOH), 0.25 g La catalyst (0.05 mmol La), and 10 mmol H_2O_2 (50 wt%). The reaction was stirred at 20 °C. H_2O_2 concentration was determined by cerimetry [37]. Typically, 200-µl aliquots of the reaction mixture were diluted into 20 ml water containing 2 ml 7 vol% aqueous H_2SO_4. The mixture was titrated with 0.1 M $Ce(SO_4)_2 \cdot 4H_2O$ in aqueous H_2SO_4 (1 M) until the color of the solution changed to yellow.

2.4.2. Determination of the $^1O_2$ yield by chemical trapping with β-citronellol

For all catalysts, a standard activity test was carried out with β-citronellol as a substrate. A 25-ml flask was charged with 10 ml alkaline methanol (0.02 M KOH), 5 mmol citronellol, 0.25 g catalyst (0.05 mmol La), and 20 mmol H_2O_2 (50 wt%). The reaction mixture was stirred at 20 °C for 24 h. Reaction of $^1O_2$ with β-citronellol yields an equimolar mixture of isomeric allylic hydroperoxides. Before GC analysis, the excess H_2O_2 and the hydroperoxide products were reduced to the corresponding alcohols with the use of excess trimethylphosphine, $(CH_3)_3P$ (1 M), in tetrahydrofuran (THF). This reduction step is fast and quantitative. GC analysis indicated that the two allylic alcohols of β-citronellol were the sole products, and, unless stated otherwise, other probable by-products, such as the diastereomeric epoxides, were not formed. For GC analysis, a Hewlett-Packard 5890 gas chromatograph equipped with a 0.32 mm i.d. × 50 m WCOT fused silica column coated with a Chrompack CP-Sil 5 CB stationary phase (1.2 µm d_f) was used. The instrument was equipped with a flame ionization detector (FID) and was coupled to a HP 3396 integrator. We quantified the reaction products by taking into account appropriate response factors.

2.4.3. Peroxidation of olefinic compounds

The general procedure for the peroxidation of olefinic compounds was as follows. A 25-ml flask was charged with 5 ml alkaline methanol (0.04 M KOH), 5 mmol olefin, 0.25 g La-USY (0.05 mmol La), and 20–50 mmol H_2O_2 (50 wt%). For the more hydrophobic olefins, 10 ml methanol (0.02 M KOH) was used. The reaction mixture was stirred at 40 °C, and the reaction progress was followed by GC analysis of the crude reaction mixture after centrifugation and reduction with excess $(CH_3)_3P$.

Products were identified by GC-MS, by ^1H and ^{13}C NMR, and by comparison of their GC retention times with those of authentic allylic hydroperoxides or allylic alcohols prepared by photochemical oxidation in the presence of *meso*-tetraphenylporphyrin (chloroform) or rose bengal (methanol) as a photosensitizer. In these photooxidations, the reaction mixture was irradiated with light from a Schott KL-1500 fiberoptics cold light source. The solution was kept under an oxygen atmosphere at 0 °C. For GC-MS analysis, a Fisons GC 8000 series gas chromatograph equipped with a 0.32 mm i.d. × 60 m WCOT fused silica column coated with a Varian CP-Sil 5 CB Low bleed/MS stationary phase (0.25 µm d_f) was coupled to a Fisons MD 800 mass spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 and 75 MHz, respectively.

2.4.4. *Heterogeneity test*

To check the heterogeneous nature of the observed catalysis, a conventional filtration test was carried out [38]. At 5–10% conversion of β-citronellol, the catalyst was separated from the reaction mixture by centrifugation, and the reaction progress in the filtrate and in the catalyst suspension was further monitored by GC analysis.

3. Results and discussion

3.1. *Catalyst screening*

The catalytic activity and H_2O_2 efficiency of lanthanum(III) immobilized on various supports were studied in three ways. First, the ability of the catalysts to disproportionate H_2O_2 was evaluated. Next, the production of $^1O_2$ from H_2O_2 disproportionation was measured indirectly by its reaction with citronellol as a chemical trap. In a third approach the $^1O_2$ yield was determined by the direct detection of the chemiluminescence of $^1O_2$.

3.1.1. *Disproportionation of H_2O_2*

Preliminary experiments indicated that the presence of a catalytic amount of a base such as KOH is necessary for the observation of any activity of the La catalysts in the disproportionation of H_2O_2. A typical reaction was carried out in the presence of 5 mM La immobilized on a support and 1 M H_2O_2 (50 wt%). Methanol containing KOH (0.02 M) was used as the solvent, and the reaction mixture was stirred at 20 °C. Some typical kinetic profiles of the disproportionation of H_2O_2 in the presence of a support, Na-Y, and the actual catalyst, LaNa-Y, are shown in Fig. 1. In the absence of base, the decomposition of H_2O_2 was almost negligible. Initial H_2O_2 disproportionation rates were calculated from the initial linear region of the $[H_2O_2]$ versus time plots. For the data points in Fig. 1, values of 22 and 1 $\mu M\,s^{-1}$ were calculated for LaNa-Y and Na-Y, respectively. Clearly, the highest rate was observed for the La-exchanged zeolite, and the contribution of the support or the base to the disproportionation of H_2O_2 or to the generation of $^1O_2$ was negligible.

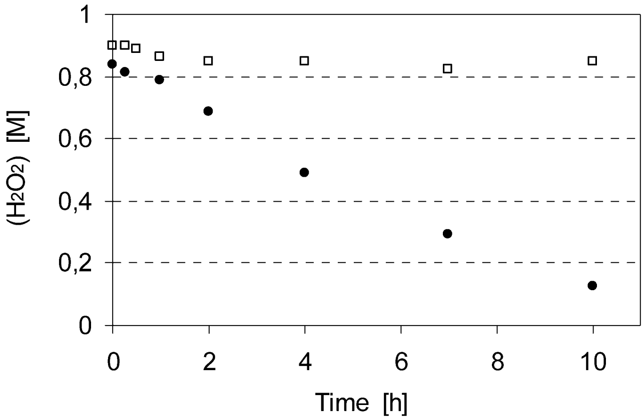


Fig. 1. Disproportionation of H_2O_2 in the presence of Na-Y (□) and LaNa-Y (●). Reaction conditions: 0.25 g Na-Y or LaNa-Y (0.05 mmol La), 10 ml 0.02 M KOH in MeOH, 10 mmol H_2O_2 (50 wt%), 20 °C.

Table 2
H_2O_2 disproportionation and citronellol peroxidation catalyzed by La-catalysts

Entry	Catalyst	H_2O_2 disproportionation, initial rate[a] ($\mu M\,s^{-1}$)	Citronellol peroxidation, yield (24 h)[b] (%)
1	LaNa-mordenite	2	0
2	LaNa-deal. mordenite	–[c]	3
3	LaNa-L	5	0
4	LaNa-A	8	0
5	LaNa-Y	22	1
6	*Na-Y*	1	–[c]
7	LaNa-ZSM-5	30	5
8	LaNa-montmorillonite	67	9
9	*Na-montmorillonite*	15	–[c]
10	LaNa-laponite	–[c]	20
11	LaNa-Amberlyst 15	10	15
12	LaNa-USY	33	45
13	LaNa-Beta	38	43
14	$La(OH)_3$	0.2	2[d]
15	La_2O_3	< 0.2	2[d]
16	$La(NO_3)_3$	17	20[d]

[a] Reaction conditions: 0.05 mmol La (0.25 g La-zeolite), 10 ml MeOH (0.02 M KOH), 10 mmol H_2O_2 (50 wt%), 20 °C.

[b] Same conditions but 5 mmol citronellol, 20 mmol H_2O_2, 24 h. GC analysis after reduction with excess $(CH_3)_3P$. Selectivity to allylic hydroperoxides > 95% in all cases.

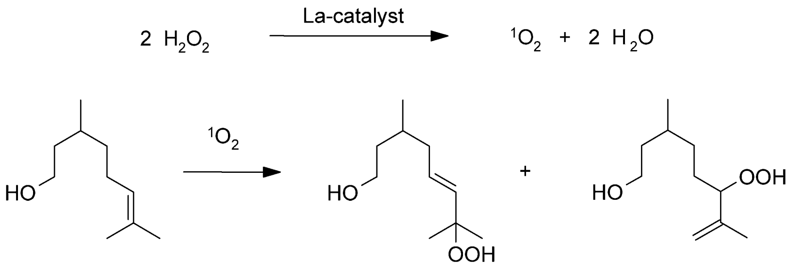
[c] Not determined.

[d] Incomplete H_2O_2 disproportionation.

In the same way as for LaNa-Y, the initial rates of H_2O_2 disproportionation by the other La catalysts were calculated. These data are compiled in Table 2.

3.1.2. *Determination of the $^1O_2$ yield by chemical trapping with citronellol*

In the presence of citronellol as an olefinic substrate, two consecutive reactions may take place in the present system: the La-catalyzed disproportionation of H_2O_2 into $^1O_2$ and the subsequent reaction of $^1O_2$ with citronellol. The latter



Scheme 1. Generation of $^1O_2$ and its reaction with citronellol.

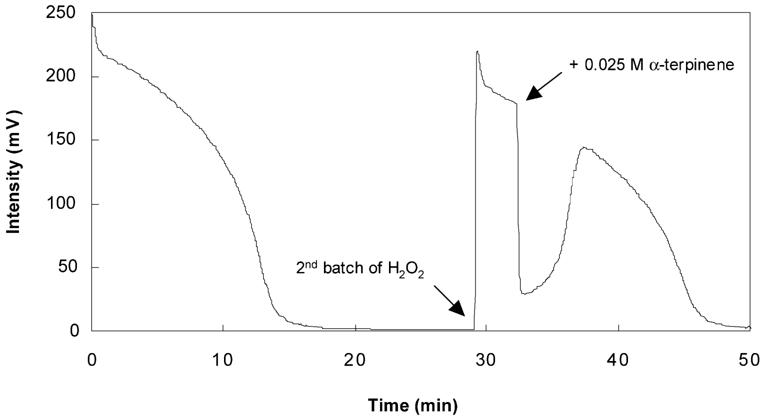


Fig. 2. Chemiluminescence signal of $^1O_2$ generated from a suspension containing 2 g LaK-USY (0.04 M La) and H_2O_2 (0.4 M, two batches) in methanol, in the presence of NaOH (0.1 M) at 35 °C.

reaction does not require intervention of a catalyst. An almost equimolar mixture of isomeric allylic hydroperoxides is formed. These products and the product distribution are characteristic for the peroxidation of citronellol via a $^1O_2$ oxidation pathway (Scheme 1).

Alternatively, the formed $^1O_2$ may be converted to $^3O_2$ via quenching by the solvent or via physical quenching by citronellol. Moreover, some part of $^1O_2$ may be quenched by collision with the support. The results of the peroxidation of citronellol by various La catalysts are compiled in Table 2. The reported yields correspond to the total yield of the two allylic hydroperoxides after 24 h of reaction. In all cases selectivity for allylic hydroperoxides was near 100%, and no epoxides were formed. The hydroperoxide yield was taken as a measure for the $^1O_2$ yield. As a consequence of the above-mentioned quenching processes, the actual total $^1O_2$ yield will always be higher than that determined by the chemical reaction of $^1O_2$ with citronellol.

3.1.3. *Determination of the $^1O_2$ yield by chemiluminescence measurements*

The infrared luminescence of the weak radiative transition of $^1O_2$ at 1270 nm was used as specific and unequivocal proof for the formation of singlet ($^1\Delta_g$) molecular oxygen in the disproportionation of H_2O_2 catalyzed by La zeolites, and it indicates that other reaction pathways do not contribute significantly to the decomposition of H_2O_2 [39,40]

$$^1O_2\left(^1\Delta_g\right) \rightarrow {}^3O_2\left(^3\Sigma_g{}^-\right) + h\nu \text{ (1270 nm)}.$$

Table 3
Assessment of $^1O_2$ yield of La-catalysts by chemiluminescence measurements[a]

Entry	Catalyst	I_p[b] (mV)	t_{end}[c] (min)	$^1O_2$ yield (%)
1	LaNa-mordenite	9.2	76	0
2	LaNa-ZSM-5	3.2	48	0
3	LaNa-Amberlyst 15	10	29	0
4	LaNa-Y	40	23	18
5	LaNa-montmorillonite	36	18	19
6	LaNa-Beta	112	26	27
7	LaNa-USY	220	14	50

[a] Reaction conditions: 4 g La-catalyst (0.2 mmol La/g), 1 ml NaOH (2 M), 500 µl H_2O_2 (50 wt%), 20 ml MeOH, 35 °C.

[b] I_p, maximum intensity.

[c] t_{end}, total reaction time. Error, ±5% of the stated values.

By recording this signal as a function of time, we determined the total $^1O_2$ yield. We calibrated the signal by adding a $^1O_2$-trapping agent to the reaction mixture. α-Terpinene was chosen as a $^1O_2$ trap since it reacts almost quantitatively with $^1O_2$ toward the cyclic peroxide ascaridole. Addition of α-terpinene leads to a decrease in the area in Fig. 2. From a comparison of the missing area with the total area recorded in the absence of α-terpinene, the cumulated amount of $^1O_2$ can be calculated. For each catalyst, the maximum intensity (I_p) of the signal, the reaction time (t_{end}), and the area under the curve were determined (Table 3). The maximum intensity of the signal is related to the rate of $^1O_2$ generation, and the total area is related to the total yield of singlet oxygen.

3.1.4. Discussion

According to their activity in the disproportionation of H_2O_2 and the peroxidation of citronellol (Table 2), the La catalysts can be divided into three groups. A first series, comprising LaNa zeolites mordenite, L and A, shows negligible or very low activity in the disproportionation of H_2O_2 (entries 1–4). This may be related to the small pores or the one-dimensional pore system of the zeolites. Furthermore, unfavorable location of La within the zeolite might affect the activity. In this respect it is interesting to note that calcination of active La zeolites (e.g., LaNa-USY) strongly reduced the activity. A key parameter controlling the location of La in zeolites is the degree of hydration of the La^{3+} cation [29,31]. The large diameter of the hydration sphere of the La cations prevents their access to, for example, the sodalite cages of zeolite Y. When the La-zeolite is heated, the trivalent cations are partly dehydrated and might migrate to positions in which coordination of H_2O_2 with La is less favored.

A second group includes La catalysts (LaNa-montmorillonite, zeolites LaNa-Y and LaNa-ZSM-5) showing an appreciable activity in the disproportionation of H_2O_2 but only a low conversion of citronellol (entries 5–9). This might be due to H_2O_2 decomposition via a different route, such as homolytic decomposition by metal impurities. For example, montmorillonite contains small amounts of iron. The relatively high decomposition activity of the parent support compared with that of the actual La catalyst corroborates this idea (entries 8 and 9). Another explanation for the low hydroperoxide yield could be the hindered access of citronellol to the pores due to steric hindrance or to polarity mismatching. In such a case, most of the $^1O_2$ produced will be quenched by collision with the solvent or with the zeolite.

For this second series of catalysts, valuable information on the generation of $^1O_2$ can be obtained from the direct detection of $^1O_2$ by means of chemiluminescence measurements (Table 3). This technique eliminates the disadvantages inherent in the use of probe molecules such as citronellol. In Fig. 3, the $^1O_2$ yield obtained by chemical trapping of $^1O_2$ with citronellol and the yield obtained by chemiluminescence measurements are compared for the various La catalysts. Although the reaction conditions are slightly different for the two experiments, the same trend is observed. The only exception is LaNa-Y. Although only a very low hydroperoxide yield is observed for LaNa-Y, the chemiluminescence measurement shows that a substantial amount of $^1O_2$ is formed. This means that $^1O_2$ is produced indeed, but it cannot react efficiently with citronellol because of enhanced quenching of $^1O_2$ within the zeolite or the low concentration of citronellol within the zeolite pores as a consequence of polarity differences. Finally, in accordance with the above-mentioned discussion, Fig. 3 shows that the $^1O_2$ yields assessed by chemical trapping are systematically lower than those determined by chemiluminescence measurements.

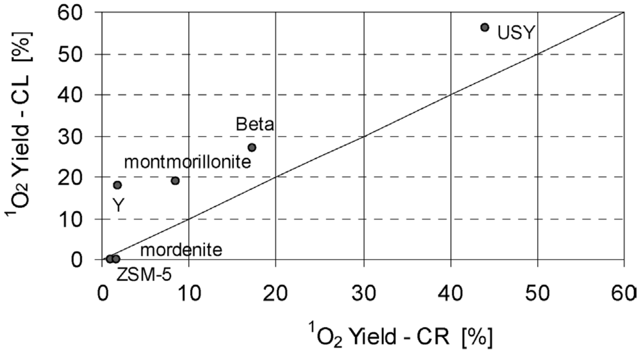


Fig. 3. Comparison of $^1O_2$ yield produced by La-catalysts and H_2O_2 as determined by chemiluminescence (CL) and chemical reaction (CR) with citronellol. Similar reaction conditions as in Tables 2 and 3. Different catalyst batches were used in comparison with Table 2.

The third series comprises La catalysts showing a relatively high activity in both disproportionation and peroxidation (Table 2, entries 10–13). LaNa-Beta and especially LaNa-USY give the highest yield of citronellol hydroperoxides. The large difference in hydroperoxide yield between LaNa-Y (entry 5) and LaNa-USY (entry 12) is striking. Zeolite Beta has a large external surface area, and both zeolite Beta and USY have a three-dimensional intersecting pore system with 12-membered ring micropores or with mesopores. Both factors likely favor the access of citronellol to the close proximity of the $^1O_2$ producing centers or, alternatively, the easy escape of $^1O_2$ from the zeolite interior to the solution containing citronellol. In contrast to the polar Y zeolite ($Si/Al = 2.7$), the USY and Beta zeolites used in this work typically have a Si/Al ratio of 10–15 (Table 1). This suggests that differences in adsorption properties for H_2O_2 and citronellol might be important as well.

Finally, in contrast to zeolite-supported La, unsupported La, such as commercial $La(OH)_3$ (entry 14) and La_2O_3 (entry 15), displays very low activity in both the absence and presence of added base, whereas La-hydroxide prepared in situ by the addition of NaOH to La-nitrate shows reasonable activity (entry 16). However, the observed activity is at most half of that of the most active La zeolites, and the efficiency at complete H_2O_2 conversion is 5–10% less.

3.2. Optimization of La-USY

The preliminary screening experiments (Table 2) showed that LaNa-USY is the most promising catalyst for the disproportionation of H_2O_2 into $^1O_2$. Therefore, further optimization of this catalyst was carried out. La-USY zeolites with various Si/Al ratios were tested, and the influence of the immobilization technique on the activity was studied.

3.2.1. Influence of the Si/Al molar ratio of La-USY

USY zeolites with various Si-to-Al molar ratios (Si/Al) were exchanged with a limited amount of La (0.05 mmol La/g). The activity of the La-USY catalysts in the disproportionation of H_2O_2 was determined (Fig. 4). On the other

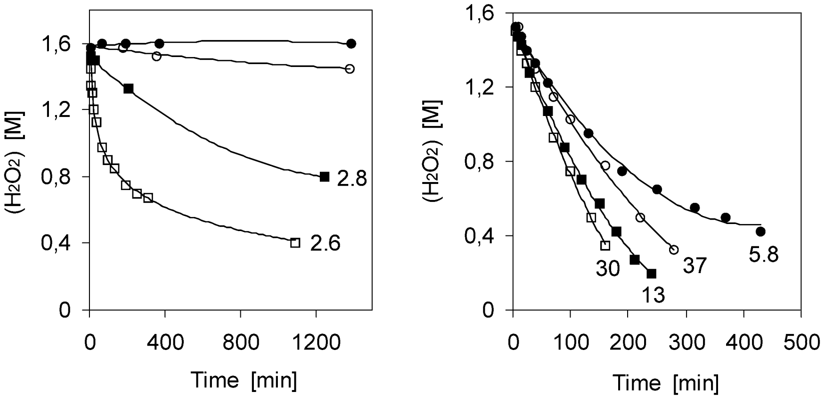


Fig. 4. Kinetic profiles of the H_2O_2 disproportionation by LaK-(US)Y zeolites. Left: no CBV (●), K-CBV720 (○), LaK-CBV600 (■), LaK-CBV100 (□). Right: LaK-CBV712 (●), LaK-CBV780 (○), LaK-CBV720 (■), LaK-CBV760 (□). No CBV, without La and without USY; K-CBV720, K-USY without La. Data labels show the Si/Al ratio. Reaction conditions: 0.25 g LaK-zeolite (0.0125 mmol La, 0.05 mmol La/g), 2.5 mmol H_2O_2 (50 wt%), 5 ml 0.01 M KOH in MeOH, 40 °C.

Table 4
Peroxidation of citronellol with LaK-(US)Y zeolites and H_2O_2[a]

Entry	Catalyst	Si/Al[b]	Yield (24 h) (%)
1	LaK-CBV100	2.6	2.0[c]
2	LaK-CBV600	2.8	11.5[c]
3	LaK-CBV712	5.8	25.3[c]
4	LaK-CBV720	13	29.2
5	LaK-CBV760	30	30.0
6	LaK-CBV780	37	31.6

[a] Reaction conditions: 0.25 g LaK-(US)Y (0.0125 mmol La, 0.05 mmol La/g), 2.5 mmol citronellol, 5 mmol H_2O_2 (50 wt%), 5 ml 0.01 M KOH in MeOH, 40 °C.

[b] Bulk analysis, determined by ICP [35,36].

[c] Incomplete H_2O_2 decomposition.

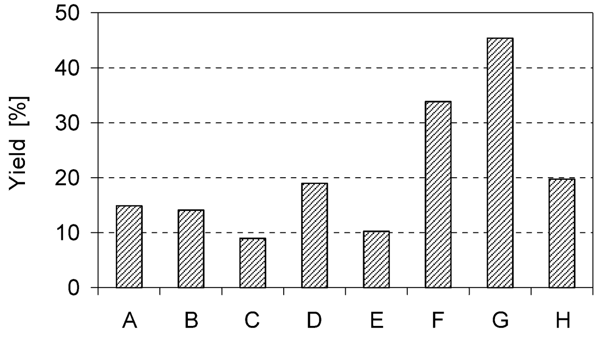


Fig. 5. Influence of the preparation conditions of La-USY (CBV-720) on the peroxidation of citronellol with H_2O_2. (A) Solid-state exchange of H-USY with $LaCl_3$ (3 h at 550 °C), (B) impregnation of H-USY with $LaCl_3$ (ethanol, 20 °C), (C) treatment B followed by calcination (3 h at 550 °C), (D) ion exchange of H-USY with $LaCl_3$ (24 h at 70 °C), (E) treatment D followed by calcination, (F) ion exchange of H-USY with $La(NO_3)_3$, (G) ion exchange of Na-USY with $La(NO_3)_3$, (H) treatment G followed by calcination. Reaction conditions: 0.25 g La-USY (0.05 mmol La), 5 mmol citronellol, 10 ml 0.02 M KOH in MeOH, 20 mmol H_2O_2 (50 wt%), 20 °C, 24 h.

hand, the efficiency of H_2O_2 use of these catalysts was evaluated with the peroxidation of citronellol as a test reaction. Results are shown in Table 4. Zeolites with a low Si/Al ratio showed a low activity in the disproportionation of H_2O_2, and, accordingly, the yield of citronellol hydroperoxides was low. On the other hand, zeolites with a high Si/Al ratio showed both a high H_2O_2 disproportionation rate and a high yield of hydroperoxides. The lower activity of LaK-CBV780 might be due to the limited cation exchange capacity of this zeolite, resulting in a La loading lower than 0.05 mmol/g. Thus, the most active and efficient catalysts with a reasonable cation exchange capacity are LaK-USY zeolites with a Si/Al ratio of 15–30.

3.2.2. *Influence of catalyst preparation conditions*

Lanthanum(III) was immobilized on USY zeolite (CBV-720) by three different techniques: solid-state ion exchange, impregnation, and conventional ion exchange. These techniques may influence the dispersion and location of La on the support. La-chloride and La-nitrate were used as the La precursor, and the zeolite was in the proton or sodium form (H-USY or Na-USY). As shown in Fig. 5 for $LaCl_3$, conventional ion exchange (D) gives slightly better results in the peroxidation of citronellol compared with solid-state ion exchange (A) and impregnation (B). This might be related to the presence of a large number of easily accessible La sites in the ion-exchanged sample, whereas in the sample prepared by solid-state ion exchange (3 h at 550 °C), La might partly migrate to less accessible sites. Compared with impregnation, conventional ion exchange might lead to a better dispersion of La on the surface of the zeolite, which would result in a higher activity. Calcination (3 h at 550 °C) of the impregnated (C) or ion-exchanged (E) samples results in a significant drop in activity, and the yields are comparable to those obtained with the sample prepared by solid-state ion exchange. Therefore, for further experiments the ion-exchanged samples were dried at low temperature (40–60 °C). By employing $La(NO_3)_3$ as the La precursor for conventional ion exchange (F), we obtained higher yields compared with the use of $LaCl_3$. For all further experiments La-nitrate was used. On the other hand, use of Na-USY (G) instead of the H-USY support gives the highest yield of citronellol hydroperoxides. This might be related to the amount of base (KOH) in the system: in the case of H-USY, KOH will be partly used to neutralize the acid sites on the zeolite surface, and the amount of KOH that can react with La^{3+} to form the catalytically active La-hydroxide will be lower. Calcination of the LaNa-USY catalyst (H) again lowers the activity, but to a lesser extent than observed for the other calcined samples. It was also observed that La-USY catalysts prepared from K-USY instead of Na-USY gave slightly higher yields. In accordance with this observation, the use of KOH as a base gave slightly better yield as compared with NaOH.

In conclusion, the most active La catalyst was obtained by conventional ion exchange of La-nitrate on K-USY zeolite as the support. After ion exchange, the catalyst was dried at relatively low temperature (40 °C).

3.3. *Optimization of reaction conditions*

After having identified LaK-USY (Si/Al = 15, 0.2 mmol La/g, conventional ion exchange of K-USY at 70 °C, drying at 40 °C) as the most active and efficient La catalyst for the generation of $^1O_2$, the most important reaction parameters were optimized. The influence of the amount of base, the solvent, and the reaction temperature was studied.

3.3.1. *Influence of the amount of base*

As already mentioned, an essential feature of the La-zeolite/H_2O_2 system is the need for slightly alkaline pH conditions. In neutral or acidic medium, no disproportionation of H_2O_2 is observed. The amount of base added to the reaction medium has been optimized. As shown in Fig. 6, there is a clear optimum at 0.03 M KOH. This corresponds to a La/OH^- molar ratio of 1/6. At lower base concentration, H_2O_2 disproportionation is slow. At too high a base concentration, the base-induced, unproductive decomposition predominates, and yields of $^1O_2$ products decrease again. The rates of H_2O_2 disproportionation at KOH concentrations of 0.02, 0.05, and 0.1 M were 47, 80, and 107 μM s^{-1}, respectively. At higher temperatures it might be advisable to use a smaller amount of base (e.g., 0.02 M KOH) in order to minimize the amount of H_2O_2 lost by unproductive H_2O_2 decomposition.

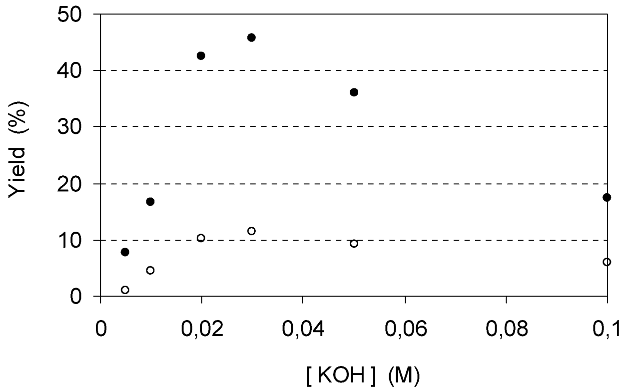


Fig. 6. Influence of the amount of base on the peroxidation of citronellol with H_2O_2 and LaNa-USY after 4 h (○) and 24 h (●) reaction. Reaction conditions: 0.25 g LaNa-USY (0.05 mmol La), 5 mmol citronellol, 10 ml MeOH, 20 mmol H_2O_2 (50 wt%), 20 °C.

The base may play at least a dual role in the reaction. First, some of the hydroxide anions will react with lanthanum cations, yielding partially or fully hydrolyzed La species on the zeolite surface [41–45]

$$La^{3+} + x OH^- \rightarrow La(OH)_x{}^{(3-x)+}.$$

Second, the base may facilitate coordination of H_2O_2 on lanthanum by converting H_2O_2 to the more nucleophilic hydroperoxide anion. Hydroxide anions also can neutralize residual acidic sites on the zeolite surface. Moreover, the alkaline pH conditions are beneficial for the stability of the allylic hydroperoxide products during the reaction and during workup. Indeed, under acidic pH conditions, allylic hydroperoxides may undergo rearrangement and decomposition reactions that do not occur under neutral or basic conditions [46].

3.3.2. *Influence of the solvent*

The solvent may play an important role, since it can influence both the rate of H_2O_2 disproportionation and the lifetime of $^1O_2$. Therefore, various solvents were tested in the peroxidation of citronellol with LaNa-USY/H_2O_2. Hydroperoxide yields after 24 h of reaction are reported in Fig. 7. Small-sized, polar solvents such as methanol and acetonitrile gave the highest yield of citronellol hydroperoxides. However, no clear correlation was found between solvent parameters or $^1O_2$ lifetime and the hydroperoxide yield [47]. This can be due to the presence of a substantial amount of water in the present system, which decreases the $^1O_2$ lifetime. At higher temperatures (40 °C), the reaction in acetonitrile was less selective (90% selectivity) because of epoxidation via intermediately formed peroxycarboximidic

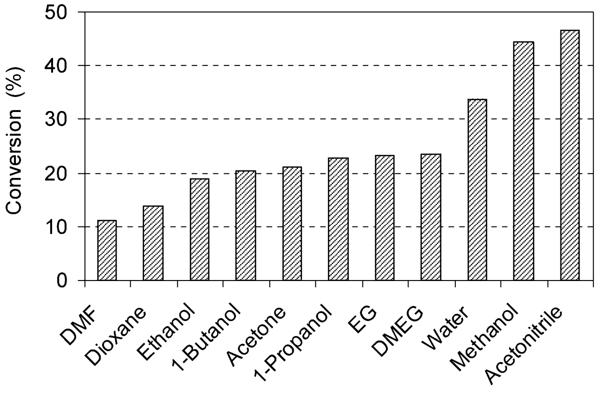


Fig. 7. Influence of the solvent on the peroxidation of citronellol with H_2O_2 and LaNa-USY. Reaction conditions: 0.25 g LaNa-USY (0.05 mmol La), 10 ml solvent, 0.2 ml 1 M NaOH in water, 5 mmol citronellol, 20 mmol H_2O_2 (50 wt%), 20 °C, 24 h. Selectivity to hydroperoxides > 95% in all cases. DMF, *N*,*N*-dimethylformamide; EG, ethylene glycol; DMEG, ethylene glycol dimethyl ether.

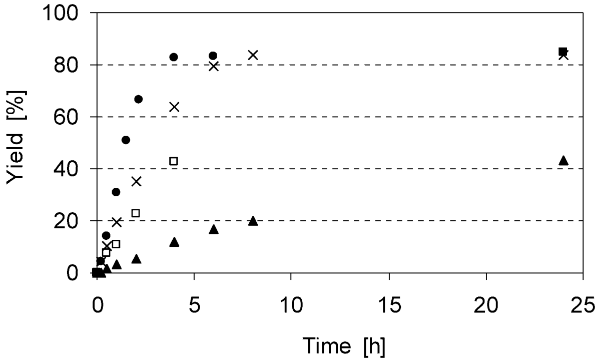


Fig. 8. Influence of the reaction temperature on the peroxidation of citronellol with H_2O_2 and LaNa-USY: 25 °C (▲), 40 °C (□), 50 °C (×), 60 °C (●). Reaction conditions: 0.25 g LaNa-USY (0.05 mmol La), 5 mmol citronellol, 10 ml 0.02 M KOH in MeOH, 40 mmol H_2O_2 (50 wt%).

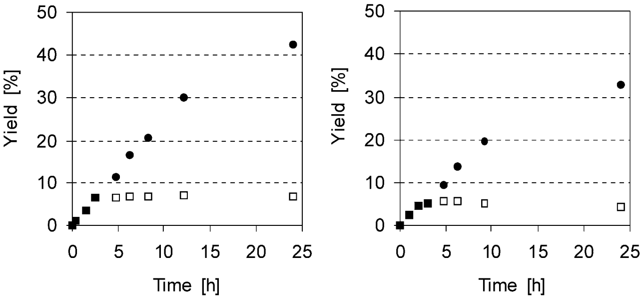


Fig. 9. Hydroperoxide yield as a function of time in the suspension (●) with LaNa-USY (left) or La-nitrate (right) and in the filtrate (□) after catalyst removal. Reaction conditions: 0.25 g LaNa-USY (0.05 mmol La) or 0.05 mmol $La(NO_3)_3$, 5 mmol citronellol, 10 ml 0.02 M KOH in MeOH, 20 mmol H_2O_2 (50 wt%), 20 °C.

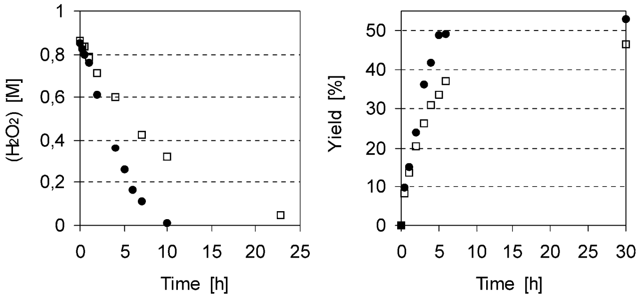


Fig. 10. Comparison of La-nitrate (□) and LaNa-USY (●) in the disproportionation of H_2O_2 (left) and the peroxidation of citronellol (right). Reaction conditions (H_2O_2 disproportionation): 0.25 g LaNa-USY (0.05 mmol La) or 0.05 mmol $La(NO_3)_3$, 10 ml 0.02 M KOH in MeOH, 10 mmol H_2O_2 (50 wt%), 20 °C. Reaction conditions (citronellol peroxidation): 0.25 g LaK-USY or 0.05 mmol $La(NO_3)_3$, 5 mmol citronellol, 10 ml 0.02 M KOH in MeOH, 20 mmol H_2O_2 (50 wt%), 40 °C.

acid, a well-known stoichiometric oxidant for olefin epoxidation [48]. Not surprisingly, GC analysis showed the presence of acetamide in the reaction mixture. Interestingly, the use of water as the solvent resulted in a rather high yield, although water and citronellol are not macroscopically miscible. For this reaction, extra methanol was added at the end of the reaction to obtain a homogeneous solution before GC analysis. In view of the latter result, the peroxidation of citronellol in the absence of a solvent was attempted. A high yield (85%) was obtained with La-USY and 8 equivalents of H_2O_2 relative to citronellol. In contrast, with La-nitrate as the catalyst, a much lower yield (15%) of citronellol hydroperoxides was obtained at complete H_2O_2 conversion. This result may indicate the selective adsorption of citronellol in the zeolite pores or on the surface, where it can react with released $^1O_2$.

3.3.3. Influence of the reaction temperature

The peroxidation of citronellol with La-USY/H_2O_2 was studied at temperatures ranging from 25 to 60 °C (Fig. 8). As expected, activity increased with increasing temperature. At 60 °C, a maximum yield of 80% was reached after 4 h of reaction. Interestingly, no decrease in H_2O_2 efficiency was noticed at the higher temperatures, and no side products were detected.

3.4. Heterogeneity and comparison of La-USY with unsupported La

To check the heterogeneity of the LaNa-USY catalyst, we carried out a heterogeneity test. As shown in Fig. 9, no further reaction was observed in the supernatant after the catalyst was removed by centrifugation. In addition, it is shown that the precipitate formed upon the addition of NaOH to La-nitrate also behaves as a heterogeneous catalyst [18].

Next, the activity and efficiency of unsupported lanthanum and LaNa-USY were compared (Fig. 10 and Table 2; entries 12–16). LaNa-USY shows a high rate in the disproportionation of H_2O_2, whereas the rate of La-nitrate tends to decrease as a function of time. Accordingly, it takes a much shorter time to obtain maximum conversion of citronellol with LaNa-USY. Maximum conversion at 20 °C is reached after 10 h for LaNa-USY, whereas it takes more than 24 h to obtain complete H_2O_2 disproportionation with La-nitrate.

This difference in activity may be related to the larger number of accessible La sites on the zeolite surface, whereas in the La-hydroxide gel, a significant amount of La is buried in the gel matrix. Next to enhanced site isolation, the improved activity might be due to the electrostatic field exerted by the zeolite framework [49], which may destabilize the La–O_2 and O–O bonds in the peroxo-La complexes. In addition to the higher activity and higher H_2O_2 efficiency, another advantage of zeolite-supported lanthanum is the high mechanical strength of the catalyst. This simplifies separation of the catalyst by filtration or centrifugation and ensures stable activity in time. In contrast, this is less straightforward for an ill-defined La-hydroxide gel whose structure and activity might alter upon drying.

3.5. Catalyst stability and reusability

To evaluate the stability of the catalyst under the alkaline pH conditions used, X-ray powder diffraction patterns

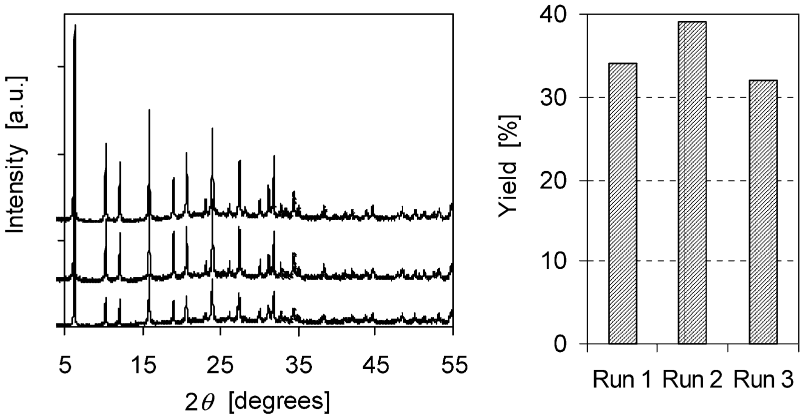


Fig. 11. X-ray diffraction patterns (left) of K-USY (top), LaK-USY (middle), and LaK-USY after three runs (bottom). Reuse (right) of LaNa-USY in the peroxidation of citronellol. Reaction conditions: 0.25 g LaNa-USY (0.05 mmol La), 5 mmol citronellol, 10 ml 0.02 M KOH in MeOH, 20 mmol H_2O_2 (50 wt%), 20 °C, 24 h.

were recorded before and after repeated use of LaK-USY (CBV-720) in the peroxidation of citronellol. As shown in Fig. 11, no appreciable changes are noticed in comparison with the parent K-USY zeolite. Therefore, the zeolite structure remains unaffected under the reaction conditions. The decrease in signal intensity that occurs in going from K-USY to LaK-USY can be explained in terms of the enhanced adsorption of X-rays by La cations. LaNa-USY was reused in three subsequent reactions. After each run, the catalyst was separated by centrifugation, washed three times with methanol, and dried at 60 °C. As shown in Fig. 11, no appreciable decrease in activity or efficiency was observed.

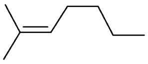
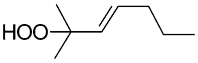
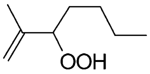
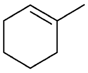
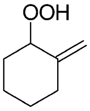
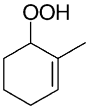
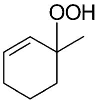
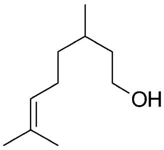
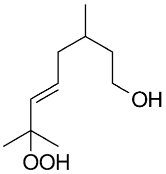
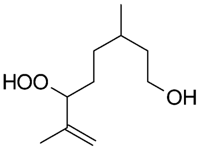
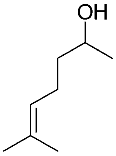
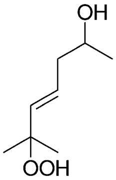
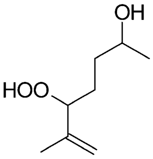
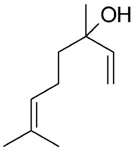
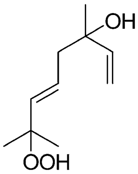
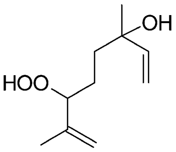
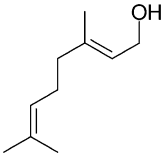
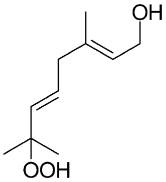
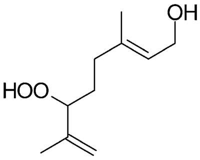
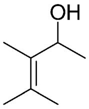
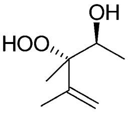
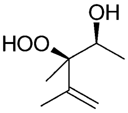
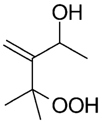
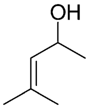
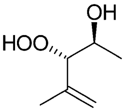
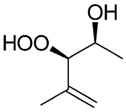
3.6. Peroxidation of olefinic compounds with H_2O_2 and LaK-USY

Under the optimized conditions, LaK-USY was used for the peroxidation of various olefinic compounds (Table 5). Alkyl-substituted alkenes react with $^1O_2$ via the so-called ene or Schenck reaction, and mixtures of regioisomeric allylic hydroperoxides with a unique product distribution are obtained [50,51]. This is illustrated by the peroxidation of 2-methyl-2-heptene (Table 5, entry 1). This substrate typically requires 6 eq of H_2O_2 to achieve complete conversion. The selectivity of the reaction of $^1O_2$ generated by La-USY/ H_2O_2 is similar to that of known solution photochemistry. Thus, the regioselectivity-sensitive probe 1-methyl-1-cyclohexene (entry 2) gave a hydroperoxide mixture showing the same product distribution as that observed for photooxidations in isotropic media [52]. In contrast, recent reports on the photooxygenation of alkenes within sensitizer dye-exchanged zeolites show product distributions that are drastically influenced by the zeolite microenvironment [53–58]. In these studies large amounts of zeolite were used relative to the amount of substrate (e.g., 5 mg alkene per 300 mg of zeolite). In contrast, in the present study a much higher substrate-to-zeolite ratio was used, and the aqueous reaction conditions used may have prevented close cation-olefin interactions. Alternatively, this may mean that the largest part of $^1O_2$ escapes into solution and then reacts with the dissolved substrate [59]. The observed product distribution significantly differs from that of other types of oxidation, such as oxidation by radical species, and thus provides additional evidence that $^1O_2$ is the main oxidizing species [52].

Oxyfunctionalized alkenes such as the monoterpene citronellol (entry 3) cleanly yielded the allylic hydroperoxide products, with no oxidation of the primary alcohol observed. For comparison, the oxidation of citronellol with $La(OH)_3$ requires at least 12 eq of H_2O_2 to fully convert citronellol, versus only 8 eq with the La zeolite [18]. Photooxidation of citronellol is the first step in the preparation of rose oxide, an important perfumery ingredient [4,60,61]. Secondary alcohol groups such as those present in 6-methyl-5-hepten-2-ol were also inert under the reaction conditions (entry 4). For linalool (entry 5) and geraniol (entry 6), two monoterpenes containing allylic alcohol functionalities, regioselective peroxidation occurred at the isolated, electron-rich 6,7-double bond. In the case of linalool, no peroxidation or epoxidation of the less electron-rich, allylic double bond was observed. Whereas no epoxidation occurred at the allylic 2,3-double bond of geraniol, some peroxidation of this double bond was observed, especially at high substrate conversions.

Finally, La-USY/H_2O_2 was used for the oxidation of allylic alcohols to the corresponding hydroperoxy homoallylic alcohols [62–65]. Subsequent reduction of the hydroperoxide functionality yields the enediols [66–71]. This is illustrated by the peroxidation of 3,4-dimethyl-3-penten-2-ol (entry 7) and 4-methyl-3-penten-2-ol (mesitylol, entry 8). The oxidation proceeded with high chemoselectivity toward the hydroperoxide products, and very little epoxidation and no alcohol oxidation were observed. In contrast, conventional Mo catalysts show much lower selectivity in the $^1O_2$ oxidation of allylic alcohols because of competing epoxidation [18]. More generally, an advantage of La over Mo is that the rate of $^1O_2$ formation is independent of the H_2O_2 concentration, whereas in the case of Mo the concentration has to be carefully controlled to maintain optimum activity and to suppress competitive epoxidation.

Table 5
Peroxidation of olefinic compounds with LaK-USY/H_2O_2[a]

Substrate	Products Distribution (%)			H_2O_2 (eq)	Conversion (%)	Selectivity (%)
 **1**	 46		 54	8	98	99
 **2**	 34	 19	 47	10	98	97
 **3**	 47		 53	8	99	97
 **4**	 46		 54	8	97	99
 **5**	 44		 56	8	98	99
 **6**	 46		 54	8	92	82
 **7**	 41[b]	 13[b]	 46	4	87	88
 **8**	 76[b]		 24[b]	10	51	94

[a] Reaction conditions: 0.25 g LaK-USY (0.05 mmol La), 5 mmol olefin, 5 ml MeOH (0.04 M KOH), 20–50 mmol H_2O_2 (50 wt%), 40 °C, 24 h. Entries 1–2: 10 ml MeOH (0.02 M KOH). GC analysis after centrifugation and reduction with excess $(CH_3)_3P$.

[b] Pair of enantiomers.

4. Conclusions

In conclusion, it was shown that lanthanum(III)-exchanged zeolites USY and Beta are active, selective, and efficient catalysts for the generation of $^1O_2$ from H_2O_2. A small crystal size, a large external surface, and a three-dimensional intersecting pore system with large pores allow a high rate of $^1O_2$ generation and an efficient reaction of $^1O_2$ with olefinic compounds. These properties also explain the superior performance of La zeolites compared with unsupported La. For some applications, such as the peroxidation of allylic alcohols, the La catalysts show superior selectivity compared with conventional Mo catalysts.

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