

Lanthanum-exchanged zeolites as active and selective catalysts for the generation of singlet oxygen from hydrogen peroxide

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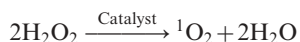
Received (in Cambridge, UK) 23rd September 2004, Accepted 28th October 2004

First published as an Advance Article on the web 17th December 2004

DOI: 10.1039/b414597f

Lanthanum(III)-exchanged zeolites Beta and USY are active and selective catalysts for the generation of singlet oxygen from H₂O₂ showing superior activity and oxidant efficiency compared to unsupported La-catalysts, e.g. La(OH)₃.

Reaction of H₂O₂ with certain metal ions produces peroxometal species capable of eliminating molecular oxygen in the lowest excited electronic state or singlet delta (¹Δ_g) state:¹



In particular, molybdate (MoO₄²⁻) is an active catalyst for the disproportionation of H₂O₂ into ¹O₂ and its synthetic utility for the peroxidation of olefins has been investigated.² However, a major disadvantage of Mo is the low selectivity in the oxidation of allylic alcohols.³ This is due to the enhanced tendency of allylic alcohols to undergo epoxidation *via* direct oxygen-atom transfer from peroxo-Mo species.⁴ Moreover, in the oxidation of secondary allylic alcohols, enone formation might compete.

Recently, some of us reported the use of lanthanum(III) and H₂O₂ for the ¹O₂ oxidation of allylic alcohols.³ The reaction is highly selective since peroxo-La species themselves are poor oxidants. Disadvantages of the La/H₂O₂ system, however, are the lower activity and lower H₂O₂ efficiency in comparison with Mo/H₂O₂. These drawbacks may be related to the appearance of the active catalyst as a dense La-oxo/hydroxo precipitate, which may cause mass transfer limitations. The latter is important in view of the short lifetime of ¹O₂ (e.g. 4.5 μs in water). In addition, the presence of numerous O–H bonds in the La-oxide/hydroxide may induce enhanced quenching of ¹O₂.⁵ We now show that certain La-exchanged zeolites have high activity and high oxidant efficiency in the generation and utilization of ¹O₂ from H₂O₂.

Lanthanum-zeolites (2.5 wt.% La) were prepared by partial ion exchange of the corresponding Na-zeolites with La(III)-nitrate.† The H₂O₂ disproportionation rates of zeolite-supported and unsupported La were determined by cerimetry and the amount of ¹O₂ formed was assessed by chemical trapping of ¹O₂ with citronellol. This olefin contains two types of allylic hydrogen atoms and reacts with ¹O₂ to yield an equimolar mixture of allylic hydroperoxides.

Table 1 indicates that the activity of the LaNa-zeolites is strongly dependent on the zeolite topology and composition.‡ According to their activity in the disproportionation of H₂O₂ and the peroxidation of citronellol, the LaNa-zeolites 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 H₂O₂. This may be related to the small pores

or the one-dimensional pore system. Also, unfavourable location of La within the zeolite might affect the activity. A second group includes LaNa-zeolites (Y, ZSM-5) showing an appreciable activity in the disproportionation of H₂O₂ but only a low conversion of citronellol. This might be due to H₂O₂ decomposition *via* a different route, e.g. homolytic decomposition by metal impurities such as iron. Another explanation for the low hydroperoxide yield could be the hindered access of citronellol to the pores due to steric hindrance or to polarity mismatch. In such a case, most of the produced ¹O₂ will be quenched by collision with the solvent or with the zeolite. This might be of particular relevance for zeolites with a large crystal size. The third series comprises LaNa-zeolites (Beta, ultrastable Y) showing high activity in both the disproportionation and peroxidation. Zeolite Beta and ultrastable Y zeolite both have a three-dimensional intersecting pore system with 12-membered ring micropores or with mesopores. Moreover, especially zeolite Beta possesses a very small crystal size. Both factors likely favour the access of citronellol to the ¹O₂-producing centres, or alternatively, the easy escape of ¹O₂ from the zeolite interior to the solution containing citronellol. In contrast to the polar Y zeolite, the USY and Beta zeolites have a Si to Al ratio of 10–15.† This suggests that differences in adsorption properties for H₂O₂ and citronellol might be important as well.

In contrast to zeolite-supported La, unsupported La-catalysts such as commercially available La(OH)₃ and La₂O₃ displayed very low activity both in the absence or presence of added base, whereas La-hydroxide prepared *in situ* by adding NaOH or KOH to La-nitrate showed reasonable activity.³ However, the observed

Table 1 Activity of La-catalysts in the disproportionation of H₂O₂ and the peroxidation of citronellol

Catalyst	Initial rate of H ₂ O ₂ disproportionation ^a /μM s ⁻¹	Hydroperoxide yield ^b (%)
LaNa-mordenite	2	0
LaNa-L	5	0
LaNa-A	8	0
LaNa-Y	22	1
LaNa-ZSM-5	30	5
LaNa-Beta	38	43
LaNa-USY	33	45
La(OH) ₃	0.2	2 ^c
La ₂ O ₃	<0.2	2 ^c
La(NO ₃) ₃	17	20 ^c

^a Reaction conditions: 0.05 mmol La (0.25 g LaNa-zeolite), 10 mL methanol (0.02 M KOH), 10 mmol H₂O₂ (50 wt.%), 20 °C. ^b Same conditions but 5 mmol citronellol, 20 mmol H₂O₂, 24 h. GC analysis after reduction with excess (CH₃)₃P. Selectivity to allylic hydroperoxides > 95% in all cases. ^c Incomplete H₂O₂ disproportionation.

activity was at most half of that of the most active La-zeolites and the efficiency at complete H₂O₂ conversion was 5–10% less. The improved activity and efficiency of zeolites such as LaNa-USY and LaNa-Beta are attributed to a high dispersion of La which results in a large number of accessible La sites. This might allow higher diffusion rates and could lower the amount of ¹O₂ lost by quenching. Next to enhanced site isolation, the improved activity might be due to the electrostatic field exerted by the zeolite framework, which may destabilize the La–O₂ and O–O bonds in the peroxy-La complex.





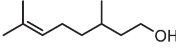
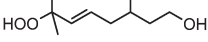
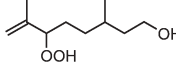
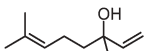
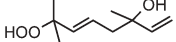
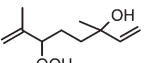







Selected examples of the peroxidation of various olefinic compounds with LaK-USY/H₂O₂ are shown in Table 2. Olefins containing different allylic hydrogen atoms such as 1-methyl cyclohex-1-ene gave allylic hydroperoxide mixtures with the same product distribution as observed for photooxidations in isotropic media (Entry 1).[§] Thus, in contrast to recent reports on intrazeolite photooxidation, no deviation from the normal product distribution was observed.⁶ This may be ascribed to the high substrate to zeolite ratio used in this work and to the aqueous reaction conditions, which prevent close cation–olefin interactions. Alternatively, this may mean that the largest part of ¹O₂ escapes into solution and then reacts with the dissolved substrate. Other olefins such as citronellol and linalool gave the allylic hydroperoxides in excellent yields (Entries 2–3). For comparison, the oxidation of citronellol with La(OH)₃ requires at least 12 equivalents of H₂O₂ to fully convert citronellol, vs. only eight equivalents with the zeolite.³ Photooxidation of citronellol is the initial step in the preparation of rose oxide, an important perfumery ingredient.⁷ For linalool, regioselective peroxidation occurred at

the electron-rich 6,7-double bond. No peroxidation of the less electron-rich, allylic double bond was observed. Finally, La-USY was used for the oxidation of allylic alcohols to the corresponding hydroperoxy homoallylic alcohols (Entries 4–5).⁸ The oxidation proceeded highly selectively towards the hydroperoxides; very little epoxidation and no alcohol oxidation were observed. In contrast, molybdate shows much lower selectivity for this transformation (e.g. 40% selectivity for Entry 5 with MoO₄²⁻/H₂O₂ in methanol).³

The LaK-USY catalyst could be easily separated from the reaction mixture and was reused three times without appreciable loss of activity. In order to check the heterogeneous nature of the observed catalysis, a filtration test was carried out. At low conversion of citronellol (5%), LaK-USY was separated from the reaction mixture and the reaction progress in the filtrate and in the catalyst suspension was further monitored by GC analysis. No further reaction occurred in the filtrate, whereas the conversion in the catalyst suspension increased from 5 to 40%. X-ray diffraction patterns, recorded before and after consecutive reactions, showed that the crystallinity of the zeolite is retained, indicating that the zeolite structure remains unaffected under the reaction conditions. From a reaction engineering viewpoint, the La-zeolite/H₂O₂ system appears a viable synthetic method since the dispersion of La on a rigid support leads to stable activity in time. Moreover, the zeolite crystals are much easier to filtrate than the ill-defined La-hydroxide gel.

In conclusion, La-exchanged zeolites Beta and USY are active, selective, and efficient catalysts for the generation of ¹O₂. Further studies to elucidate the exact role of the support and the nature of the catalytically active La species are in progress.

Table 2 Peroxidation of olefinic compounds with ¹O₂ generated from LaK-USY/H₂O₂^a

Entry	Substrate	H ₂ O ₂ /equiv.	Products	Distribution (%)	Conversion (%)	Selectivity (%)
1 ^b		10	  	34 : 19 : 47	98	97
2		8	 	47 : 53	99	97
3		8	 	44 : 56	98	99
4		4	  	41 : 13 : 46	87	88
5		10	 	76 : 24	51	94

^a Reaction conditions: 5 mL methanol (0.04 M KOH), 5 mmol olefin, 0.25 g LaK-USY (0.05 mmol La), 20–50 mmol H₂O₂ (50 wt.%), 40 °C, 24 h. GC analysis after centrifugation and reduction with excess (CH₃)₃P. Products were identified by GC-MS, ¹H and ¹³C NMR and by comparison with authentic samples prepared by photooxidation with tetraphenylporphyrin (CHCl₃) or rose bengal (CH₃OH) as photosensitizer. **CAUTION:** H₂O₂ solutions are strongly oxidizing and should be handled with appropriate precautions. Commercial 30 and 50 wt.% H₂O₂ could be used with similar results. ^b Methanol, 10 mL (0.02 M KOH).

We thank the EC (SUSTOX project, GIRD-CT-2000-00347) and the Belgian Federal Government (IUAP-PAI project on Supramolecular Chemistry and Catalysis) for financial support.

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Notes and references

† LaNa- or LaK-zeolites (2.5 wt.% La) were prepared by stirring Na- or K-zeolites (10 g) in 0.5 L of an aqueous solution of La(NO₃)₃·6H₂O (2 mmol) for 24 h at 70 °C. After ion exchange, the La-zeolites were separated by filtration, washed with distilled water, and dried at 40 °C. Zeolites used were USY (Si/Al = 13, CBV720, PQ), Beta (Si/Al = 10.8, CP811BL-25, PQ), Y (Si/Al = 2.7, Zeocat), A (Si/Al = 0.9, Zeocat), L (Si/Al = 3, EXAR109, Uetikon), ZSM-5 (Si/Al = 13, SN-27, Alsi-Penta) and mordenite (Si/Al = 5.7, Zeolon 100, Norton).

‡ Preliminary experiments showed that a catalytic amount of a base is required in order to observe any activity of La in the disproportionation of H₂O₂. Optimum activity was observed at a KOH : La molar ratio of 4 : 1.

The use of LaK-zeolites instead of LaNa-zeolites gave slightly more active catalysts. In the absence of La, no H₂O₂ decomposition took place. In addition, the Na-zeolite support itself showed no or very low decomposition activity and no oxidation products were detected in the presence of citronellol.

§ The product distribution of the oxidation of 1-methylcyclohex-1-ene confirms the involvement of ¹O₂ as opposed to radical-induced oxidation. Convincing evidence for the generation of ¹O₂ (¹Δ_g) from La-zeolites/H₂O₂ was obtained by direct detection of the near-infrared (1270 nm) chemiluminescence accompanying the radiative decay of ¹O₂.

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