Heterogeneous molybdate catalysts for the generation of singlet molecular oxygen ($^1\Delta_g$) from H_2O_2

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The immobilisation of molybdate on Mg,Al-LDH leads to an active, heterogeneous catalyst that generates singlet molecular oxygen from hydrogen peroxide in the absence of soluble base.

Molecular oxygen in the singlet state ($^1O_2$) is a unique reagent for oxyfunctionalisation, as its product distributions essentially differ from those of radical or electrophilic agents such as RO* radicals or (in)organic peracids.[1] Singlet O_2 can be generated from $^3O_2$ *via* visible excitation of dissolved or heterogenised photosensitisers (*e.g.* porphyrins or rose bengal), but the need for an efficient illumination and the photolability of many dyes are major drawbacks for scale-up of such systems.[2–5] An alternative pathway is the catalysed production of $^1O_2$ from alkaline H_2O_2.[6] Several metal ions can act as homogeneous catalysts for this reaction, in particular molybdate and calcium. This contribution presents a new solid catalyst for $^1O_2$ generation, consisting of active molybdate centers embedded in a layered double hydroxide (LDH) matrix. Such catalytic design eliminates the need for a soluble base. The production of $^1O_2$ is evidenced by spectral observations and by oxygenation of characteristic substrates.

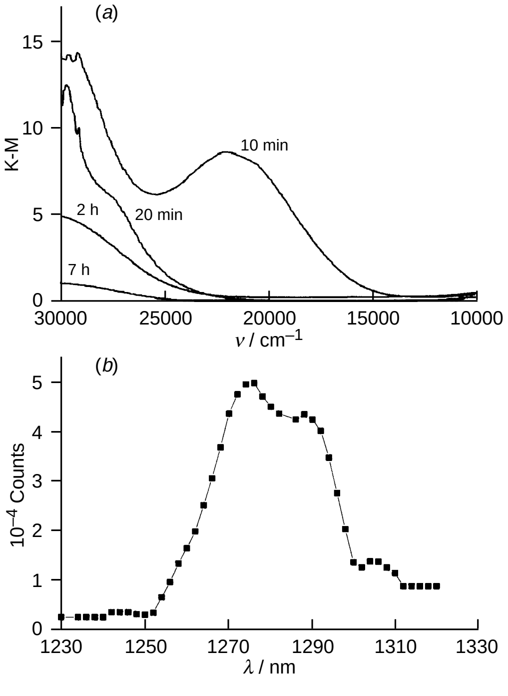
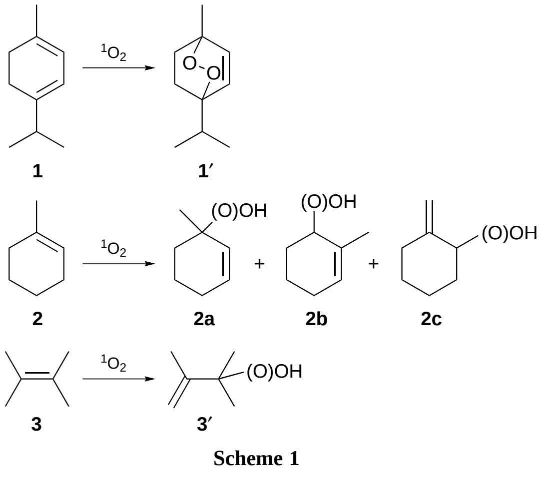


Fig. 1 Exposure of $Mg_{0.7}Al_{0.3}$-LDH-MoO_4 (37.5% AEC), suspended in 1,4-dioxane, to H_2O_2 (0.5 mmol, as 35% in water). (*a*) Diffuse reflectance UV–VIS spectrum recorded at different times after H_2O_2 addition (0.1 g LDH in 0.5 ml solvent; K–M = Kubelka–Munk). (*b*) IR luminescence spectrum, recorded with a liquid N_2 cooled Ge detector (0.025 g LDH in 1.75 ml solvent).

LDHs are analogues of the mineral hydrotalcite, and can be synthesised in a variety of elemental compositions, depending on the desired surface pH and anion exchange capacity.[7] For the present work, a $Mg_{0.7}Al_{0.3}$-LDH was precipitated in degassed water at pH 10, ion-exchanged with MoO_4^{2-} in the same conditions, and isolated by freeze-drying. A typical Mo loading of 5.5 mass% corresponds to occupation of 37.5% of the anion exchange capacity with divalent molybdate anions. When this catalyst is exposed to aqueous H_2O_2 in dioxane, the suspension turns brick-red. This colour change was studied with time-resolved diffuse reflectance spectroscopy [Fig. 1(*a*)]. Bands are observed at 330 and 450 nm. Especially the latter band is typical of polyperoxomolybdate species, *e.g.* $[MoO(O_2)_3]^{2-}$ and $[Mo(O_2)_4]^{2-}$. Such Mo species are formed in particular at high peroxide : Mo ratios and at high pH.[8] Monitoring the spectrum as a function of time shows a steady decrease of the intensity of the polyperoxo bands. This decay corresponds to the disproportionation of the peroxo groups into oxo groups and singlet oxygen, as is proved unequivocally by the near infrared luminescence spectrum. Simultaneously with the UV–VIS spectral change, an emission peak is observed at 1276 nm, which is in satisfactory agreement with the reported energy of the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transition [Fig. 1(*b*)].[9] The smooth release of $^1O_2$ and the formation of the polyperoxomolybdates are in agreement with the basic nature of the LDH surface; in solution, the same processes would require addition of additional NaOH. When the $[MoO_4]^{2-}$ exchanged LDH is removed by filtration, the H_2O_2 decomposition stops completely. This proves that the Mo is really heterogeneous, even if the singlet oxygen may diffuse into the solution.

As the production of $^1O_2$ was firmly established from the physicochemical methods, we turned to the application of the material in $^1O_2$ mediated (per)oxidations (Scheme 1).† The 1,3-diene α-terpinene (**1**) was selected as a substrate for [2π + 4π] cycloaddition; the feasibility of $^1O_2$ 'ene' type reactions was tested with 1-methylcyclohexene **2** and 2,3-dimethyl-but-



Scheme 1

Table 1 Yields for oxidations with $^1O_2$, generated from H_2O_2 by LDH-MoO_4 catalyst[a]

		Product yields (%)				
			$^1O_2$ products[d]			
Substrate	Catalyst[b]	Epoxide	**2a**	**2b**	**2c**	TON[c]
1-Methylcyclohex-1-ene	$Mg_{0.7}Al_{0.3}$-LDH-MoO_4[e]	0.6	11.7	2.3	5.0	17
	$Mg_{0.7}Al_{0.3}$-LDH-MoO_4[f]	0.6	12.4	2.9	5.4	29
	$Mg_{0.7}Al_{0.3}$-LDH-MoO_4	0.9	19.2	6.4	8.6	86
	$Mg_{0.8}Al_{0.2}$-LDH-MoO_4	0.6	23.5	4.3	11.6	98
	$Mg_{0.9}Al_{0.1}$-LDH-MoO_4	0.5	23.2 (53)[g]	7.1 (16)[g]	13.4 (31)[g]	109
	Rb[h]		(50[g]	(19)[g]	(31)[g]	
		Epoxide	$^1O_2$ products **3′**			
2,3-Dimethylbut-2-ene	$Mg_{0.7}Al_{0.3}$-LDH-MoO_4	4.7	19.6			49
	$Mg_{0.8}Al_{0.2}$-LDH-MoO_4	2.9	32.4			81
	$Mg_{0.9}Al_{0.1}$-LDH-MoO_4	2.3	47.9			120
		Endoperoxide **1′**				
α-Terpinene	$Mg_{0.7}Al_{0.3}$-LDH-MoO_4	14.4				36
	$Mg_{0.8}Al_{0.2}$-LDH-MoO_4	21.6				54
	$Mg_{0.9}Al_{0.1}$-LDH-MoO_4	24.5				61

[a] *Reaction conditions*: 2.5 mmol substrate, 5 mmol H_2O_2 35% in water, 0.05 g catalyst containing 10 μmol $[MoO_4]^{2-}$, 3 ml of 1,4-dioxane, 293 K. Product yields on substrate basis. [b] Subscripts for Mg and Al refer to molar fractions in LDH octahedral layer. [c] TON = moles of $^1O_2$ products per mol of Mo. [d] **2a** = 1-hydro(pero)xy-1-methylcyclohex-2-ene; **2b** = 1-hydro(pero)xy-2-methylcyclohex-2-ene; **2c** = 1-hydro(pero)xy-2-methylenylcyclohexane. [e] 28 μmol $[MoO_4]^{2-}$ on 0.05 g LDH, or 37.5% of the anion exchange capacity. [f] 18 μmol MoO_4^2 on 0.05 g LDH, or 25% of the anion exchange capacity. [g] Values between brackets: distribution of $^1O_2$ oxidation products (%). [h] Photosensitisation with rose bengal (3.10^{-5} M in ethanol), cold light source Schott KL 1500, 293 K.

2-ene **3** (Table 1). The endoperoxide ascaridole is obtained from **1** with a 98% selectivity. With **2** and **3**, hydroperoxide formation is accompanied by a double-bond shift, as expected for a non-free radical, $^1O_2$ mediated peroxidation. Characteristically, the double bond also shifts to the exocyclic position in the case of **2**; the product distribution is essentially the same as for a photosensitised reaction. While the recovered enols undoubtedly originate from the corresponding hydroperoxides, the only competing side reaction is a limited epoxidation. Such an epoxidation of double bonds by peroxo d^0 metals is well documented; however, in our reactions, epoxides in all cases amount to < 20% of the formed products.

A principal advantage of LDHs over other supports (*e.g.* polymers) is that the characteristics of the catalytic site's environment are easily modified. For instance, co-exchange of the LDH with $[MoO_4]^{2-}$ and an organic anion such as toluene-*p*-sulfonate (Ts) transforms the polar layered double hydroxide into a much more lipophilic material. With ($[MoO_4]^{2-}$,Ts)-LDH as a catalyst, the consumption of H_2O_2 is more gradual, which is undoubtedly due to a repulsion of the primary oxidant H_2O_2 by the apolar surface. While this catalyst modification increases the eventual conversion of *e.g.* 1-methylcyclohexene, this increase is almost totally accounted for by a fivefold multiplication of the epoxide yield. A more successful catalyst modification is the dilution of the $[MoO_4]^{2-}$ active centers over the hydrophilic support. When the occupancy of the anion exchange capacity by $[MoO_4]^{2-}$ is lowered from 37.5 to 12.5%, the yield of $^1O_2$ oxidation products almost doubles (Table 1). Apparently, a slow release of $^1O_2$ from well-dispersed active centers ensures an optimal capture of the $^1O_2$ by the organic substrate. A supplementary improvement of the catalyst is achieved by modification of the elemental composition of the LDH. Thus when the molar fraction of Al in the octahedral layer of the LDH is lowered to 10%, the epoxide formation becomes marginal, while the peroxidation yield further increases. Typically, up to 100 mol of $^1O_2$ product are formed per mol of Mo, proving that the process is truly catalytic in Mo.

Summarizing, this system is the first heterogeneous catalyst for $^1O_2$ generation from a peroxide for which the performance can be easily tuned by modification of the support. A soluble base, as required for the homogeneous molybdate system, becomes superfluous because of the basic characteristics of the LDH surface. The key to achieving high peroxidation yields is a gradual release of $^1O_2$ from a hydrophilic surface.

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Footnotes and References

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† To a mixture of the catalyst, substrate and solvent, aqueous H_2O_2 was added in two portions with an interval of 8 h. For detailed reaction conditions, see footnotes of Table 1.

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