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Letters

Alcohols oxidation with hydrogen peroxide promoted by TPAP-doped ormosils

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Abstract—Organically modified silica gels doped with TPAP (tetra-*n*-propylammonium perruthenate) are effective catalysts for the oxidation of alcohols by hydrogen peroxide at room temperature, provided that the oxidant H_2O_2 solution is added slowly. The effect of the surface catalyst polarity is the opposite of that found in aerobic alcohols oxidation and is consistent with the polar nature of the primary oxidant.

Alcohols oxidation yielding ketones and aldehydes is a chemical transformation of primary industrial importance in fine chemistry, carbonyl compounds being precursors of a variety of valuable fine chemicals including drugs, vitamins and fragrances.[1] Societal demand for fundamental chemical transformations that are not harmful to the environment is pressing, and an economically and environmentally viable replacement of traditional alcohols oxidation, still carried out by industry with stoichiometric amounts of toxic and hazardous metal oxidants such as dichromate and permanganate,[2] remains a scientific challenge for chemists both in industry and academia.[3]

Obviously, the utilization of oxygen and even better of air as stoichiometric oxidant for the selective oxidation of organics is the final, ideal goal of prolonged research efforts and a number of catalytic procedures for the aerobic alcohols oxidation employing Ru,[4] Pd,[5] Cu,[6] Co,[7] V,[8] Os[9] derivatives have been reported in the last few years. Most of these methods, however, suffer from some drawback, and in most cases either relatively large amounts of expensive catalysts are needed, or the stoichiometric consumption of a 'sacrificial' reactant or high reaction temperatures are required. Ruthenium, for instance, is probably the most promising metal in promoting aerobic oxidation of alcohols; in particular, the species tetra-*n*-propylammonium perruthenate (TPAP) either dissolved in solution[10] or immobilised on suitable supports[11] is a very efficient and selective catalyst for the aerial oxidation of primary, secondary, benzyl and alkyl alcohols in nonaqueous media,[12] including dense-phase carbon dioxide.[13] Most functional groups, such as carbon–carbon double bond, epoxy, indole, acetal, etc., remain unaffected by TPAP and high yields of carbonyls are isolated.[12,14] However, even though molecular oxygen is the most environmentally and economically convenient primary oxidant, its use in association with platinum-group-metals species and in particular with TPAP suffers the disadvantage of requiring high reaction temperatures ($T \geqslant 80\,°C$) in order to reoxidise the spent catalyst (formally RuO_2^-) to the native species.

On the other hand, besides oxygen a few primary oxidants, such as $S_2O_8{}^{2-}$ and $BrO_3{}^-$ in aqueous media[15] and N-methylmorpholine N-oxide in organic solvent at room temperature,[16] have been reported in association with TPAP for oxidizing alcohols catalytically; and, to the best of our knowledge, no reports on the utilization of hydrogen peroxide with TPAP appeared in the literature in spite of the fact that H_2O_2 is a clean and relatively cheap oxidant, which can now be efficiently produced in situ by direct reaction of O_2 with

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H_2 over a gold catalyst.[17] In this letter we describe the first use of H_2O_2 in association with entrapped TPAP in the catalytic oxidation of alcohols at room temperature.

We recently reported an efficient method for alcohols oxidation by molecular oxygen catalysed by TPAP-doped ormosils in $scCO_2$.[13] These solid catalysts are prepared by sol–gel entrapment of TPAP in silica glasses obtained using methyltrimethoxysylane (MTMS) and tetramethylorthosilicate (TMOS) as precursors of the final xerogel. Catalysts with various surface hydrophobicity were obtained by varying the percent of methyl-modified precursor utilised in the synthesis of the xerogels (i.e. 0%, 25%, 75% and 100% of MTMS) whereas catalytic doped glasses with different pores size and entrapment modality of TPAP were also obtained by varying the process employed for the xerogels preparation, that is, the amount of water and the presence of NaF. The results obtained in $scCO_2$ indicate that the best performing catalysts require both a high degree of surface hydrophobicity as well as high amounts of water in the sol–gel polycondensation process.[13]

In order to assess the possibility of exploiting TPAP-based catalysts in alcohols oxidation by H_2O_2, we decided to carry out some preliminary experiments utilising a mixture of the above mentioned TPAP-doped ormosils (catalytic load of 0.05 mmol TPAP/g ormosil) recycled upon oxidation experiments in $scCO_2$. The oxidations were conducted in a 10 mL jacketed reactor thermostated at 25 °C by suspending 100 mg of ormosil (0.005 mmol) in a 3 mL ether solution of benzyl alcohol (0.050 mmol) and *n*-dodecane (as internal standard, 0.022 mmol) kept under stirring. A solution of dry H_2O_2 in ether (0.14 mmol in 3.0 mL, by titration with acidic $KMnO_4$) was thus added by means of a syringe-pump at various time intervals. After completion of the oxidant addition, the reaction mixture was analysed by GLC to determine the alcohol conversion along with benzaldehyde and benzoic acid yields. Figure 1 clearly shows the marked effect of varying the velocity of hydrogen peroxide addition on the conversion of the alcohol. Indeed the quick addition of the H_2O_2 solution to the reaction mixture containing the substrate and the catalyst leads to a very low alcohol conversion (3–4%, Table 1), hydrogen peroxide decomposition being the major reaction pathway. Conversely, when the H_2O_2 solution is slowly added by means of a syringe-pump, alcohol conversions increase up to becoming almost quantitative.

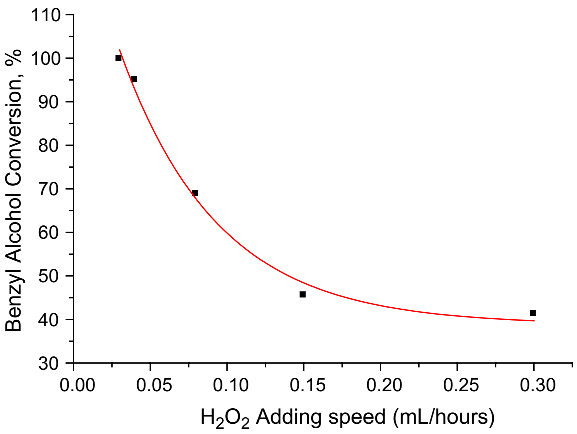

Figure 1. Benzyl alcohol conversion (0.05 mmol in 3.0 mL ether) as function of the velocity of H_2O_2 addition (3.0 mL of H_2O_2 4.7×10^{-2} M in ether) in the presence of TPAP-doped ormosils (0.005 mmol) at 25 °C.

Table 1. Benzaldehyde and benzoic acid yields as function of H_2O_2 addition velocity (3.0 mL of H_2O_2 4.7×10^{-2} M in ether) in the oxidation of benzyl alcohol (0.05 mmol in 3.0 mL of ether) in the presence of TPAP-ormosils (0.005 mmol) at 25 °C

Run	H_2O_2 Vel. add. (mL/h)	Benzyl alcohol conversion (%)	Benzaldehyde yield (%)	Benzoic acid yield (%)
1	~180[a]	4.0	4.0	—
2	0.30	41.2	41.2	—
3	0.15	45.5	45.5	—
4	0.08	68.8	67.6	1.2
5	0.04	95.0	81.8	13.2
6	0.03	99.8	26.6	73.2
7	0.03[b]	85.3	85.3	—

[a] The H_2O_2 solution was added in a single blow.
[b] In the presence of activated 3 Å molecular sieves.

These results suggest a different kinetic order in hydrogen peroxide relative to the two processes involved, namely the oxidation of the alcohol and H_2O_2 decomposition. In particular, the kinetic order for hydrogen peroxide in its decomposition catalysed by ruthenium derivatives should be higher compared to that of alcohol oxidation, so that a steeper, more pronounced dependence of the decomposition rate on the addition of the oxygen donor is observed in the former process. When the concentration of hydrogen peroxide is kept relatively low during the whole process, the alcohol is smoothly oxidised and decomposition of H_2O_2 to water and O_2 minimised.

Even the selectivity of the oxidative process is affected by the pace of hydrogen peroxide addition as shown by the data of Table 1. Hence, when alcohol conversions are lower than 50%, benzaldehyde is the only product detected (runs 1–3). At conversion higher than 50%, the alcohol overoxidation becomes significant and benzoic acid is detected along with benzaldehyde (runs 4–6). However, the overoxidation can be completely eliminated (run 7) by sequestering the water formed along with the aldehyde in the first oxidative step.

Once assessed the TPAP capability of acting as catalyst in alcohol oxidation by H_2O_2, we prepared various ormosils by sol–gel method, co-polymerising TMSO with MTMS at various ratios in the presence of TPAP in order to verify the effect of surface ormosils hydrophobicity on the catalyst activity. Thus, a catalyst prepared with 0% MTMS is essentially a complete inorganic glass whereas, a catalyst prepared with 100% MTMS is an organically modified glass bearing one methyl group each silicon atom. The results concerning

Table 2. Alcohol conversion, aldehyde and acid yields as function of catalyst methylation in the oxidation of benzyl alcohol (0.05 mmol in 3.0 mL of ether) with hydrogen peroxide (3.0 mL of H_2O_2 4.7×10^{-2} M in ether added at the velocity of 0.15 mL/h) catalysed by TPAP (0.0025 mmol) encapsulated in various MTMS/TMOS mixed gels, in the presence of 3 Å molecular sieves, at 25 °C

Run	MTMS (%)	Benzyl alcohol conversion (%)	Benzaldehyde yield (%)	Benzoic acid yield (%)
8	0	93.4	86.2	7.2
9	25	90.7	82.5	8.2
10	50	82.5	63.5	19
11	75	73.1	68.5	4.6
12	100	49.3	49.3	0
13	0[a]	99.0	72.7	26.3
14	0[b]	94.3	94.3	0
15	100[a]	51.2	51.2	0

[a] 3.0 mL of H_2O_2 4.7×10^{-2} M in ether added at the velocity of 0.04 mL/h.

[b] 3.0 mL of H_2O_2 2.3×10^{-2} M in ether added at the velocity of 0.15 mL/h.

the activity of these TPAP doped gels in the oxidation of benzyl alcohol by H_2O_2 are summarised in Table 2:

Entries 8–12 in Table 2 clearly show that the catalyst efficiency largely depends on the ormosil surface HL balance. In particular, less hydrophobic the surface, more active is the catalyst: an outcome related to the polar nature of hydrogen peroxide, which prevents its diffusion through an hydrophobic surface. Accordingly, in the aerobic alcohols oxidation mediated by these ormosils, where oxygen freely diffuses into the catalyst framework, a reverse reactivity order is observed.[11,13]

Interestingly, the selectivity of the process also depends on the catalyst hydrophobicity and only the fully methylated ormosil (run 12) completely suppresses overoxidation. A possible rationale for this behaviour, which has been observed in other catalytic applications of sol–gels,[18] is that the highly hydrophobic permethylated catalyst spills out the water formed during alcohol oxidation, thus preventing aldehyde hydration and consequently also the overoxidation to benzoic acid.

Despite the presence of molecular sieves, both the unmodified doped SiO_2 (entry 8) and the partially methylated ormosils (entries 9–11) lead to some alcohol overoxidation, thus suggesting that their drying power is comparable to that of molecular sieves. When TPAP-doped silica is the catalyst, a decrease in the speed of H_2O_2 addition affords higher alcohol conversion (run 13 compared to run 8); in this case, however, the excess of hydrogen peroxide employed yields a lower benzaldehyde selectivity.

The speed of H_2O_2 addition has a much lower effect when the TPAP-doped fully methylated silica is the catalyst, the selectivity to carbonyl remaining excellent (run 15 compared to run 12). Finally, an almost quantitative alcohol conversion and an excellent aldehyde selectivity can be obtained with TPAP-doped unmodified SiO_2 by simply reducing the hydrogen peroxide excess (run 14). Results in Table 3 prove also the generality of the method. Contrary to crystalline catalytic materials such as zeolites (including zeolite X[19a] and MCM-41[19b] doped with perruthenate, which are intrinsically shape selective), ormosils are amorphous materials showing a distribution of inner porosities, which allows their application to the conversion of largely different substrates including, in this case, long-chain aliphatic alcohols such as octanol.

The catalyst could be reused: when the oxidation of benzyl alcohol was repeated twice utilising the same mixture of catalyst and molecular sieves, and simply after filtering and washing the powder (runs 17–18), benzaldehyde was produced in lesser but yields compared to the first run. We ascribe the decreasing in aldehyde yields and the slight increasing in acid formation to the impossibility of separate and recover completely all the catalyst from the crushed and inactivated molecular sieves.

Similarly to aerobic TPAP mediated oxidations, primary alcohol functionality revealed to be more reactive than secondary alcohols both in the case of alkyl and benzyl alcohols. Remarkably, however, alkyl alcohols are only slightly less reactive than benzyl alcohols; while the lower selectivity measured in the oxidation of primary alkyl alcohol, in its turn, might be related to a greater extent of hydratation in the case of the aliphatic aldehyde compared with that of the aromatic aldehyde. The oxidation of the allylic alcohol geraniol (run 22)

Table 3. Alcohol conversions and corresponding carbonyl compounds yields in the oxidation of various alcohols (0.05 mmol in 3.0 mL of ether) with hydrogen peroxide (3.0 mL of H_2O_2 2.3×10^{-2} M in ether added at the velocity of 0.15 mL/h) catalysed by TPAP (0.0025 mmol) encapsulated in pure silica (0% MTMS) in the presence of 3 Å molecular sieves, at 25 °C

Entry	Substrate	Alcohol conversion (%)	Carbonyl compound yield (%)	Carboxylic acid yield (%)
16	Benzyl alcohol	94.3	94.3	0
17	Benzyl alcohol[a]	70.2	69.7	0.5
18	Benzyl alcohol[b]	65.4	63.9	1.5
19	(±)-1-Phenylethanol	63.3	63.0	0
20	1-Octanol	71.6	41.7	29.9
21	(±)-2-Octanol	58.9	58.9	0
22	Geraniol	62.9	25.5	37.4
23	Furfuryl alcohol	40.0	11.3	28.7
24	Borneol	20.0	20.0	0

[a] First catalyst recycling.

[b] Second catalyst recycling.

proceeds with fair yield and involves only the alcoholic function. In fact, neither the 2,3-allylic or 6,7-olefinic carbon–carbon double bonds undergo oxidation. Furfuryl alcohol too (run 23) leads to a fair conversion being the corresponding acid the major product under these experimental conditions. A more sterically hindered secondary alcohol than 2-octanol, such as borneol (run 24) gives only moderate substrate conversion with an excellent selectivity for the corresponding ketone. It should be noted that these reactions have not been optimised. Higher conversions for high molecular weight alcohols and higher selectivities for aldehydes in primary alcohols oxidation should be expected by tuning opportunely the catalyst hydrophobicity and the amount of hydrogen peroxide utilised as well as the velocity of peroxide addition.

In conclusion, we have discovered that TPAP-doped organically modified silica gels are effective catalysts for the oxidation of alcohols by hydrogen peroxide at room temperature, provided that the oxidant solution is added slowly. The effect of surface catalyst hydrophobicity is opposite of that found in aerobic alcohols oxidation and is consistent with the polar nature of the H_2O_2 primary oxidant. Considering the ease of exploiting hydrogen peroxide formed in situ[17] and the unique advantages of commercial sol–gel catalytic materials,[20] these findings might open the way to the introduction of environmentally friendly and cost-effective alcohols oxidation.

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