Partial oxidation of light paraffins with hydrogen peroxide in the presence of peroxocomplexes of copper(II) hydroxide

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Methane, ethane and ethylene are oxidised by hydrogen peroxide in aqueous solutions at room temperature and atmospheric pressure in the presence of peroxocomplexes of copper(II) hydroxide; the reaction presumably proceeds by a non-radical mechanism.

Activation of light paraffins under mild conditions is a challenge for many scientists working in the field of modern catalysis. It is known that the most active and selective catalysts for the low-temperature oxidation of light paraffins are enzymes of the (mono)oxygenase type.[1] It is now well established that the catalytic cycles of Fe- and Cu-containing enzymes of the oxygenase type usually include intermediate formation of peroxocomplexes.[2,3] Numerous bi- and polynuclear complexes of Fe and Cu with rather sophisticated organic ligands have been synthesised (see, *e.g.*, review[4]) for the structural modelling of these enzymes. However, only some of these proved to be capable of forming peroxocomplexes under mild conditions. It was recently shown that simple compounds, such as copper and iron hydroxides with polynuclear structures, can form peroxocomplexes active in the oxidation of hydrazine derivatives.[5]

The present work demonstrates for the first time the oxidation of methane, ethane and ethylene by hydrogen peroxide under mild conditions in the presence of copper(II) peroxocomplexes in a simple heterogeneous system based on $Cu(OH)_2$ deposited on SiO_2.

Equipment. A Shimadzu UV 300 spectrophotometer, a Bruker MSL 400 NMR spectrometer, a Tsvet 530 gas chromatograph with a flame ionisation detector (a 3 m column with 2% diglycerol on Carbopack) and a I-135 pH-meter were used in this work.

The reaction was carried out in 10 ml of aqueous solution in the presence of 0.5 g of a catalyst at 298 K under atmospheric pressure. The gas phase of the reactor was formed by 150 cm^3 of either air or a hydrocarbon. The volume of oxygen evolved was measured with a volumetric set-up.

The catalyst $Cu(OH)_2/SiO_2$ was prepared according to the method reported by Elizarova *et al*.[5] 50 cm^3 of water were added to 5 g of a KSKG silica gel (Dzerzhinsk, Russia) (S_{sp} = 300 $m^2\ g^{-1}$), ground to a powder, and then a 1 M solution of NaOH was added to adjust to pH 10–11. Then 7.8 cm^3 of 0.2 M $Cu(NO_3)_2$ was added with vigorous stirring. The precipitate was filtered, rinsed repeatedly with water and dried first at 383 K and then at 530 K for 30-40 min. The catalyst obtained contained 2% Cu (w/w). It should be stressed that the nature of the support and the procedure used for the hydroxide preparation are of key importance for the catalytic activity of the resulting sample. Thus, considerably less active catalysts were obtained when Aerosil or TiO_2 was used as a support.

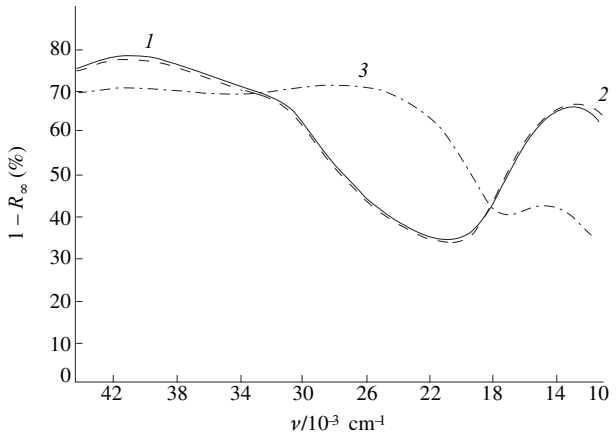

Figure 1 The diffuse reflection spectra of (*1*) bulk $Cu(OH)_2$, (*2*) $Cu(OH)_2/SiO_2$ catalyst and (*3*) the catalyst after interaction with H_2O_2.

Table 1 Products of methane, ethane and ethylene oxidation by hydrogen peroxide in the presence of $Cu(OH)_2/SiO_2$.

Substrate	pH	Concentration of H_2O_2/M	Products/10^{-3} M (in the liquid phase)
Ethane	10.6	0.15	acetaldehyde (0.63) ethanol (traces)
Ethane	8.0	0.15	acetaldehyde (1.0) ethanol (0.13)
Ethane	10.8	0.5	acetaldehyde (0.65) ethanol (traces)
Ethane	8.0	0.5	acetaldehyde (0.9) ethanol (0.11)
Ethylene	10.5	0.15	formic acid (14)
Methane	8.0	0.15	formic acid (0.08)
Methane	10.5	0.15	formic acid (0.07)

Comparison of the diffuse reflection spectrum of the catalyst with the spectrum of bulk $Cu(OH)_2$, which was prepared by the standard procedure,[6] indicated that all the copper in the catalyst system was in the hydroxide form (Figure 1). Addition of H_2O_2 to an aqueous suspension of $Cu(OH)_2/SiO_2$ rapidly turns the blue colour of the latter into brown. The diffuse reflection spectrum of the H_2O_2-treated and filtered sample exhibits a charge transfer band at 26000 cm^{-1} (Figure 1), which points to the coordination of H_2O_2 by Cu ions. This is also confirmed by the characteristic reaction with Ti^{IV}. Thus, treatment of the catalyst with a solution of Ti^{IV} in 1 M H_2SO_4 results in decomposition of the copper peroxide (disappearance of brown colour) and binding of the H_2O_2 released to Ti^{IV} with the appearance of the yellow colour of Ti^{IV} peroxocomplex.[7]

Decomposition of hydrogen peroxide in the presence of light hydrocarbons. $Cu(OH)_2/SiO_2$ is an active catalyst for the decomposition of H_2O_2 in the pH range 7–11 (dissolution of copper hydroxide takes place below pH 7). The kinetics of H_2O_2 decomposition and dioxygen evolution at pH 10.5 are shown in Figures 2 and 3, respectively. Part of the experimental evidence proves a non-radical mechanism of H_2O_2 decomposition in the presence of Cu^{II} hydroxide.[8] In particular, in the presence of radical inhibitors (- and -naphthols), neither an induction period nor a decrease in the hydrogen peroxide decomposition rate are observed in the range of inhibitor concentrations from 1.0×10^{-5} to 5×10^{-4} M.

When the hydrogen peroxide decomposition proceeds in an atmosphere of ethane or ethylene, the reaction rate is considerably lower than that in air (Figures 2 and 3). The amount of oxygen evolved also decreases. Meanwhile, the catalyst has a brown colour and thus remains in the form of peroxocomplex both in a hydrocarbon and in an air atmosphere. It is thus likely that peroxocomplexes of copper hydroxide, active in the H_2O_2 decomposition reaction, can also interact with ethane and

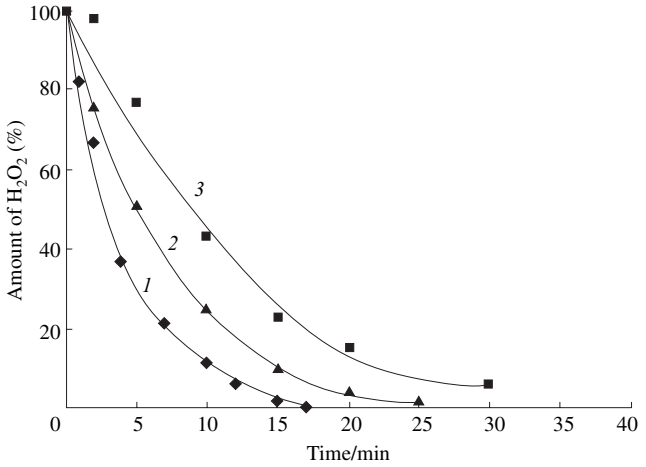

Figure 2 Kinetics of H_2O_2 (10 ml, 0.15 M) decomposition at 293 K in the presence of $Cu(OH)_2/SiO_2$ (0.5 g) at pH 10.5 in an atmosphere of: (*1*) air, (*2*) ethane and (*3*) ethylene. H_2O_2 content is given as a percentage of its initial concentration.

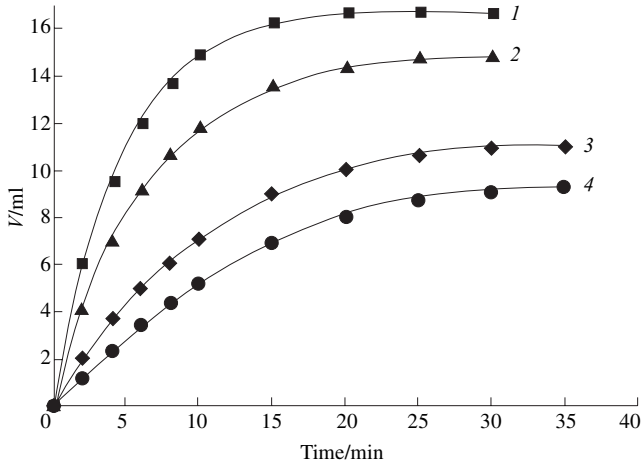

Figure 3 Kinetics of the gas evolution from 10 ml of 0.15 M H_2O_2 solution in the presence of $Cu(OH)_2/SiO_2$ (0.5 g) at pH 10.5 and 293 K in H_2O in an atmosphere of: (*1*) air, (*2*) ethane, (*3*) ethylene and (*4*) the same as (*3*) but in D_2O.

ethylene. In a methane atmosphere, the H_2O_2 decomposition in the presence of $Cu(OH)_2/SiO_2$ proceeds as fast as it does in air.

Analysis of the oxidation products. Gas chromatographic analysis of the liquid phase after complete decomposition of H_2O_2 in the presence of ethane (duration of experiment *ca.* 1 h) revealed acetaldehyde and ethanol which were undetectable in the absence of any of the reaction mixture components (catalyst, hydrocarbon or H_2O_2). The amount of products depends on the reaction conditions (Table 1). The maximum level of the ethane oxidation products in the solution shown in Table 1 corresponds to a 1.4% conversion of H_2O_2.

Upon ethylene oxidation, traces of ethylene oxide were detected in the gas phase. ^{1}H NMR spectroscopy of the liquid phase after C_2H_4 oxidation in D_2O revealed a narrow singlet at 8.43 ppm, belonging to $HCOO^-$. The latter is confirmed by spectrophotometric analysis with chromotropic acid.[9] The formate concentration was found to be 1.4×10^{-2} M and corresponded to a 36% conversion of H_2O_2. In addition, the NMR spectrum showed a strong signal from water protons ($\delta = 0.8$ ppm) which could mask the signals from other products, *e.g.*, alcohols. However, no ethanol was detected by gas chromatography. It is noteworthy that a remarkable isotope effect is observed in D_2O (Figure 3).

Despite the fact that the presence of methane has no effect on the kinetics of H_2O_2 decomposition, its oxidation does take place, since formic acid (*ca.* 8×10^{-5} M) is detected in the solution by its reaction with chromotropic acid (the sensitivity of this method is 1×10^{-5} M HCOOH).[9]

According to preliminary data, the catalysts based on iron hydroxide are also active in the oxidation of the above-mentioned hydrocarbons. They are, however, characterised by much lower reaction rates and yields of the oxidation products.

In conclusion, it is worth mentioning that hydroxides of transition metals seem to be very promising catalysts for redox reactions in aqueous solutions. This is due to their simple synthesis, polynuclear structure and an absence of organic ligands, which are usually oxidised together with an organic substrate. Taking into account the non-radical mechanism of H_2O_2 decomposition in the presence of Cu and Fe hydroxides, one may assume that hydrocarbons are also oxidised without intermediate formation of free radicals. Although the mechanisms of the hydrocarbon oxidation reactions described in the present paper are not quite clear yet, and the yields of the of light paraffin oxidation products are not sufficiently high, the very fact of their formation and the absence of a wide range of oxidation products are remarkable, and this is another argument in favour of the non-radical mechanism of oxidation. This fact distinguishes the above-mentioned systems from the radical-chain oxidation of hydrocarbons in acidic media in the presence of Fenton ($H_2O_2 + Fe^{2+}/Fe^{3+}$) reagent (see review[10] and references therein).

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