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Copper and iron hydroxides as new catalysts for redox reactions in aqueous solutions

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Supported or colloidal Cu^{II} and Fe^{III} hydroxides catalyse the oxidation of catechol to a muconic acid derivative and of benzene to phenol in aqueous hydrogen peroxide solutions at ambient temperature.

Metal hydroxides are widely used as ion exchangers, adsorbents and collectors for impurities. However, their application as catalysts is rather scarce. Meanwhile, they are very attractive for catalysis: they exhibit a polynuclear structure and a high surface area, and they can be prepared in various forms (supported species, colloidal solutions and bulk materials). We found recently that copper and iron hydroxides can be successfully used as catalysts for the oxidation of water and light hydrocarbons[1,2] and for H_2O_2 decomposition[8,9] in aqueous solutions. In this work,[†] we found that copper and iron hydroxides catalyse benzene and catechol oxidation with H_2O_2; in the latter case, their catalytic performance is similar to that of dioxygenase enzymes.

Recently,[2] we found that H_2O_2 oxidises methane and ethylene to formic acid in the presence of a $Cu(OH)_2/SiO_2$ catalyst in aqueous solution. To clarify whether the oxidation of methane proceeds *via* the consecutive formation of methanol and formaldehyde, these compounds were used as substrates. Methanol was not oxidised, whereas formaldehyde was oxidised very slowly under the conditions of methane oxidation. This led us to an assumption that formic acid is formed from hydrocarbons *via* the transfer of two oxygen atoms to the substrate, likewise the operation of dioxygenases. To prove this assumption, catechol oxidation with H_2O_2 in the presence of copper and iron hydroxides was studied.

Catechol oxidation was carried out in Ar at 295 K with vigorous stirring in the presence of either SiO_2-supported hydroxides containing 2% Fe^{III} or Cu^{II} ions or in their colloidal solutions. We found in a special experiment that the catalytic H_2O_2 decomposition followed by O_2 formation begins only after catechol oxidation.

To monitor the kinetics in the presence of supported catalysts, the samples taken from the reaction mixture were diluted with 0.1 M H_2SO_4 to stop the oxidation reaction and centrifuged; then, the spectra were measured. The semilogarithmic plots of the kinetic curves of the catechol consumption (ln C_{cat} *vs.* time) were linear in the concentration range from 0.005 to 0.02 M, thus proving the first reaction order with respect to the substrate.

Table 1 Concentrations of phenol in aqueous benzene (*ca.* 0.02 M) solutions after 1–2 h of vigorous stirring at 295 K.

Catalyst	pH	$[H_2O_2]$/mol dm^{-3}	[PhOH]/10^4 mol dm^{-3}
$FeO(OH)/SiO_2$	12	0.025	0
	7	0.025	7
in situ FeO(OH)	12	0.025	0
	7	0.025	5
	7	0.01	3
Colloid FeO(OH)	12	0.025	0
	7	0.025	0
$Cu(OH)_2/SiO_2$	12	0.1	0
	7	0.025	traces
in situ $Cu(OH)_2$	13	0.1	0
	7	0.01	3

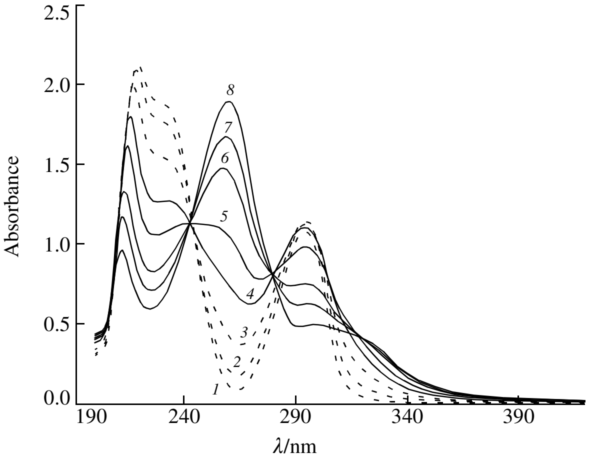

Figure 1 UV-VIS absorption spectra of the reaction mixture during the oxidation of 2×10^{-3} M catechol with H_2O_2 (7×10^{-3} mol dm^{-3}) in the presence of colloidal 1×10^{-3} mol dm^{-3} $Cu(OH)_2$ stabilised with 0.5% starch in 0.1 M NaOH at 295 K. Reaction time/min: (*1*) 2; (*2*) 5; (*3*) 10; (*4*) 15; (*5*) 20; (*6*) 25; (*7*) 30 and (*8*) 40.

The influence of the concentrations of the substrate, H_2O_2 and NaOH and the amount of a catalyst on the rate of catechol oxidation was studied. Note that the behaviours of Fe- and Cu-containing catalysts were almost identical, except for a higher activity of the latter. An increase in the NaOH concentration from 0.001 to 0.2 M accelerated the reaction by a factor of about two; the reaction rate remained nearly constant upon a further increase in the alkali concentration. In a neutral medium, the reaction was very slow. A change in the catalyst amount from 25 to 100 mg in 20 ml of the reaction mixture lead to a less than twofold increase in the oxidation rate. When the concentration of either catechol (0.005–0.05 M) or H_2O_2 (0.01–0.3 M) was varied, the reaction order changed from 1 to 0 for both of the reactants. Such orders are typical of nonradical oxidation reactions with H_2O_2.

A study of catechol oxidation in the presence of starch-stabilised hydroxide colloids supplemented these results. The reaction was studied spectrophotometrically in 0.05–0.1 M NaOH solutions in the presence of 1–5 mM catalyst. The molar ratio between catechol and a metal varied from 0.5 to 3.0, H_2O_2 concentrations changed from 0.005 to 0.025 M for each ratio. The reaction orders with respect to catechol and a catalyst equalled 1; the order with respect to H_2O_2 varied from 1 to 0 (in the same way as for the supported catalysts).

Figure 1 demonstrates the UV-VIS spectra of the reaction mixture during the catalytic oxidation of catechol in colloidal $Cu(OH)_2$. The absorption bands at 230 and 290 nm correspond to catechol absorption. The evolution of the absorption at 250 nm originates from the formation of a reaction product. The transformation of the catechol spectrum into the spectrum of the product through isosbestic points is indicative of the absence of stable intermediates. It is remarkable that an *o*-benzoquinone

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[†] *Materials and methods*. A UVIKON 923 spectrophotometer (USA), and a Kristall 2000M gas chromatograph with FID (Russia) were used; H_2O_2 was determined using Ti^{IV}.[3] Catechol absorption bands at 275 and 290 nm were used for its detection in acidic and alkaline media, respectively.

Supported $FeO(OH)/SiO_2$, $Cu(OH)_2/SiO_2$ and starch-stabilised colloidal hydroxides were prepared as described elsewhere.[1,2] In some experiments, hydroxides were obtained *in situ* by adding NaOH to copper and iron nitrates solutions.

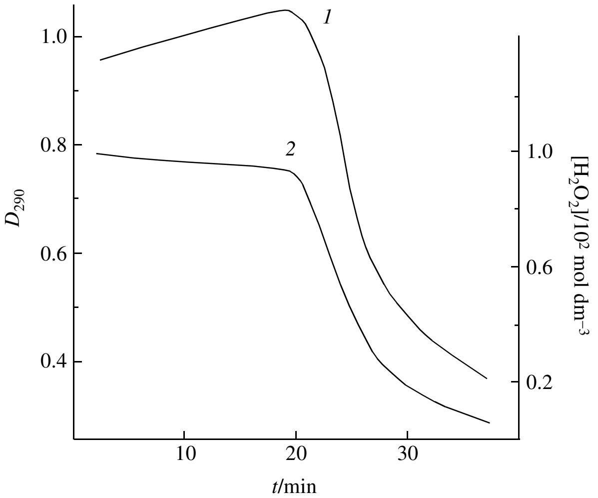

Figure 2 Kinetics of (*1*) the substrate and (*2*) H_2O_2 consumption during catechol oxidation in a colloidal FeO(OH) solution; 2×10^{-3} M catechol, 1×10^{-2} M H_2O_2, 1×10^{-3} M FeO(OH), 0.1 M NaOH, 295 K.

absorption band at 380 nm[4] was never observed. Figure 2 shows the intensity of the catechol absorption at 290 nm and the H_2O_2 concentration. Induction periods are observed in the kinetic curves, which increased with catechol concentration and decreased with H_2O_2 concentration. At a threefold excess of catechol over the catalyst and at a low H_2O_2 concentration, the oxidation rate was close to zero if catechol was added to the reaction mixture before H_2O_2, but it was rather high [especially in the case of $Cu(OH)_2$] with the reverse order of the reagent addition. This suggests a competition between the substrate and the oxidant for the sites at the catalyst active centre. The peroxide intermediate formation is likely to play a key role.

Note that the catechol absorption at 290 nm increases during the induction period (Figure 2, curve *1*); this can result from the accumulation of a complex between catechol and the catalyst. At the same time, the H_2O_2 concentration does not change, the product is not formed and the spectra of the reaction mixture do not cross the isosbestic points (dotted lines in Figure 1). We suppose that an active intermediate is formed *via* the coordination of the substrate to either a peroxo complex or metal ions in high oxidation states (Fe^{IV} or Cu^{III}).

The UV-VIS spectrum of the product does not contain the absorption band at 270–290 nm characteristic of a benzene ring, but contains a very intense absorption band at 250 nm ($\varepsilon > 10^4$ dm^3 mol^{-1} cm^{-1}), which is characteristic of muconic acid and its lactone[4] known as the products formed under the action of catechol dioxygenases. In acidic solutions, the product absorption band shifts to 225 nm, the addition of an alkali restores its position. This reversible shift of the absorption band with pH proves that the product is really an acid. Liquid chromatography (HPLC) of the working solutions and IR spectra of the samples obtained after filtration of the supported catalyst and careful drying of the supernatant evidence that the reaction product is γ-lacton of α-hydro-β-hydroxymuconic acid. The related product of di-*tret*-butylcatechol oxidation was observed previously.[5,6] Thus, copper and iron hydroxides catalyse the cleavage of a benzene ring and the transfer of two oxygen atoms, similar to catechol dioxygenases. Chemical systems modelling these enzymes have been reported.[5–7] However, this work gives the first example of the simplest inorganic catalysts acting in aqueous solutions similarly to catechol dioxygenases.

Previously,[8,9] we found that H_2O_2 decomposition in the presence of Cu and Fe hydroxides proceeds *via* a nonradical mechanism. This is due to the formation of peroxo complexes of these hydroxides and Fe^{IV} upon the interaction with H_2O_2. The rates of formation and consumption of peroxo complexes and Fe^{IV} are strongly influenced by pH, reactant concentrations and the presence of an organic substrate.[8–10] It is likely that depending on the substrate nature and/or the reaction conditions different catalyst–H_2O_2 intermediates may react with the substrate and transfer either one or two oxygen atoms to it. It was thus interesting to study the products of benzene oxidation in the presence of the hydroxide catalysts.

We found that benzene is oxidised to phenol in aqueous solutions, *i.e.*, the reaction proceeds *via* one oxygen atom transfer from the oxidant to the substrate. Table 1 lists the concentrations of phenol formed in 1–2 h in aqueous benzene (*ca.* 0.02 M) solutions under different experimental conditions. Phenol concentrations were determined either from the absorption at λ 286 nm or by GC. It is remarkable that phenol (as well as ethanol and methanol) is not oxidised in the systems under study. This is another evidence for the nonradical oxidation reaction catalysed by transition metal hydroxides.

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