were found rapidly and selectively to decompose with formation of the corresponding ketone and the starting Fe[III] complex.[14] Under the conditions used, this reaction would regenerate (tdcpp)Fe[III]–OH. The mechanism of Scheme 1 would explain the selective formation of cyclohexanone from cyclohexane and irradiated Fe(tdcpp)(OH) in catalytic amounts with the stoichiometry of eqn. (3). It would also

$$\bigcirc + O_2 + h\nu \xrightarrow{\text{Fe(tdcpp)(OH)}} \bigcirc{=}O + H_2O \qquad (3)$$
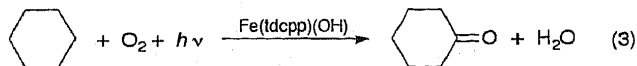
explain why this system is not able to epoxidize alkenes, as its active ·OH species is very prone to abstract hydrogen atoms from alkanes or alkenes (in allylic position) but not to add to alkene double bonds. It is noteworthy that step (a)[11] and steps (c + d)[14] have already been reported. The minor formation of alcohols from cyclohexane and cyclooctane and Fe(tdcpp)-(OH) could derive from secondary reactions due to the formation of ROO·[12] or ROOH (after steps b and c) and their further decomposition catalysed by Fe(tdcpp).[15]

This photoassisted oxidation of cyclohexane into cyclohexanone catalysed by Fe(tdcpp)(OH) is a new kind of selective activation and functionalization of alkanes by O_2 under mild conditions, as it does not need any consumption of a reducing agent in contrast with most of the previously described comparable iron porphyrin-based systems and as its mechanism better corresponds to a dioxygenase rather than to a monooxygenase reaction.

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Luminescence Experiments on Copper(I) Zeolites
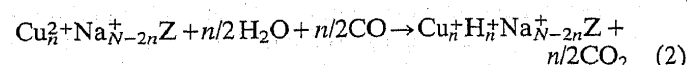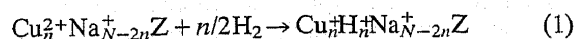
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A second band at 615 nm is observed in the luminescence spectrum of Cu^+ zeolite 4A in contrast to zeolite 13X, in which only the well known green luminescence is observed under the same conditions.

Copper(I) ions in zeolitic environments are of interest as catalysts for NO decomposition.[1] Various techniques have been devoted to investigating aspects of their reactivity. Despite the seemingly vast information provided by these experiments, fundamental questions as to the exact location of Cu^{2+} within the zeolite framework is still the subject of debate.[2] Most of the problems seem to arise because of slightly different sample history and preparation techniques. To circumvent these problems, we applied *in situ* techniques for emission spectroscopy on Cu^+ zeolites. This provides control of various parameters, such as temperature, pressure and concentration of reactants during the reduction and the measurement. Apart from the ion exchange procedure and the preparation of the wafers, manipulations were performed in a purpose-built sample chamber. Some aspects of the optical spectrum of Cu^+ zeolites have previously been reported.[3] MO studies, however, suggest a different interpretation, notably that the first electronic transition is due to a $Cu^+ \leftarrow$ zeolite–oxygen lone-pair LMCT transition.[4]

Samples with different Cu^{2+} exchange levels were prepared by ion exchange at room temperature for 3 h with aqueous solutions containing the desired amount of Cu^{2+} as $Cu(NO_3)_2$. As starting materials Na-4A (Bayer AG: Baylit T) and Na-13X (Union Carbide) were used. The exchanged zeolites were washed several times with bidistilled water, filtered, dried over night at 60 °C and then stored at 51% relative humidity. All samples, apart from zeolite 4A with more than 40% of the Na^+ exchanged for Cu^{2+}, retained their structure as checked by X-ray powder diffraction. For the measurement round wafers (13 × 1 mm) were pressed with a hardened stainless-steel die applying a pressure of 200 MPa and partially dried by evacuating them for 10 min at room temperature. Reproducibly, a pressure of 5×10^{-4} mbar was achieved. The samples were then reduced with 130 mbar of either CO or H_2 at 240 °C. Before data collection the samples were allowed to cool to room temperature. Reduction proceeded according to eqns. (1) and (2) where Z represents the negatively charged

$$Cu_n^{2+}Na_{N-2n}^+Z + n/2 H_2 \rightarrow Cu_n^+ H_n^+ Na_{N-2n}^+Z \qquad (1)$$

$$Cu_n^{2+}Na_{N-2n}^+Z + n/2 H_2O + n/2 CO \rightarrow Cu_n^+ H_n^+ Na_{N-2n}^+Z + n/2 CO_2 \qquad (2)$$

partially hydrated zeolite framework and N represents the total number of cations per pseudo unit cell.

After reduction, the samples were white or for high copper loads slightly grey. Samples dried more completely prior to the reduction, turned olive green and did not exhibit any luminescence. After each experiment, retention of the structure was checked by X-ray powder diffraction. No change in structure was found. To obtain one series of 13 individual
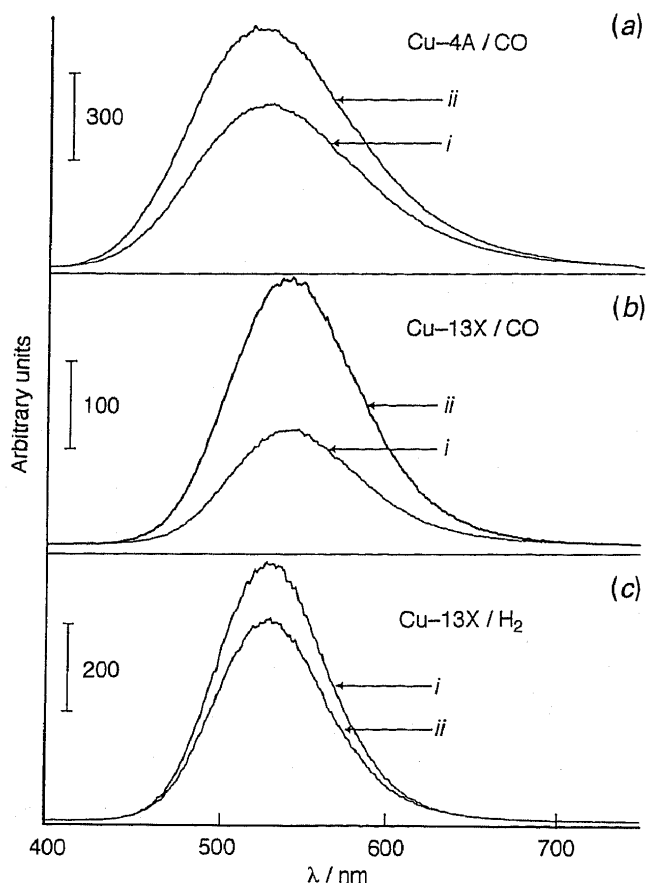
Fig. 1 Corrected luminescence spectra of Cu-4A/CO (*a*), Cu-13X/CO (*b*) and Cu-13X/H$_2$ (*c*). (*i*) Spectra prior to evacuation, (*ii*) spectra after 20 min evacuation.
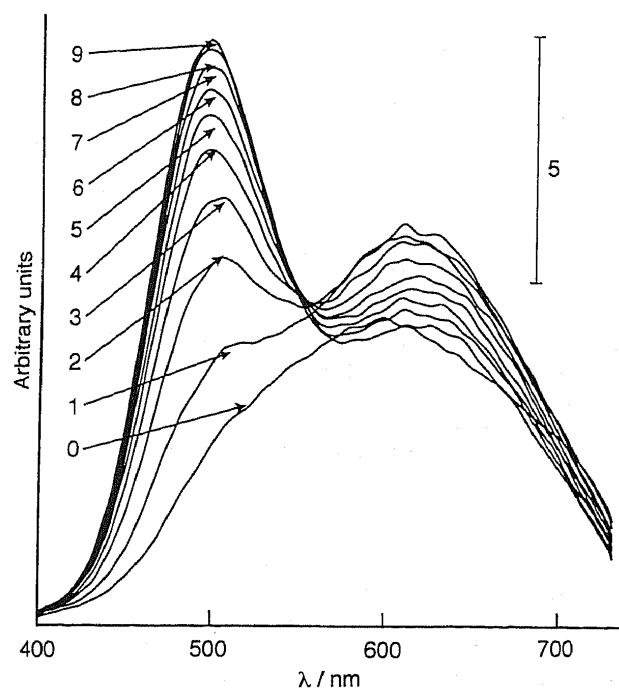

Fig. 2 Corrected luminescence spectrum of Cu-4A/H$_2$. Successive numbering denotes evacuation time/min. 0 = prior to evacuation.

emission spectra, each consisting of 250 scans, 0.08–0.16 MW cm^{-2} of the third harmonic of a Q-switched Nd:YAG laser (Continuum: YG660A) was used as excitation source and the luminescence was detected with a gated OMA III system (EG & G PARC). A gate width of 10 ms was used, a time sufficiently long to allow integration over the whole decay.[3] In Fig. 1 we report typical spectra of Cu$^+$-13X and Cu$^+$-4A, prepared by reduction for 35 min with CO (Cu-13X/CO and Cu-4A/CO) and spectra of Cu$^+$-13X, prepared by reduction for 45 min with H$_2$ (Cu-13X/H$_2$). Two spectra are presented for each sample, one in the presence of the reducing gas and one after evacuation for 20 min to a residual pressure of 10^{-5} mbar. Cu-4A/CO shows a broad asymmetric band with a maximum at 523 nm. Cu-13X/CO exhibits a less broad band centred at 540 nm. Upon evacuation, the intensity increases for both samples as expected by the removal of the quencher CO.[3] Cu-13X/H$_2$ shows an even less extended and symmetrical band at 530 nm, the intensity of which decreases upon evacuation. In CO-reduced samples, a similar decrease in luminescence intensity has been observed only after prolonged evacuation. Cu^{2+}-4A reduced with H$_2$ (Cu-4A/H$_2$), however, shows a surprisingly different behaviour, see Fig. 2. Just after reduction and prior to evacuation, a very broad, featureless band with a maximum at 615 nm and sometimes a shoulder around 515 nm is observed. Only upon evacuation does the characteristic Cu$^+$ band develop at 497 nm. The growth of this band stops after prolonged evacuation. An isosbestic point is observed at 557 nm. The second band at 615 nm can be observed in Cu-4A/CO only if the reduced sample is heated to 400 °C in dynamic vacuum. We tentatively assign this emission to small Cu$_2$O particles, formed in or on the zeolite, on the basis that Cu$_2$O is known to form under certain conditions[5] and that Cu$_2$O$_{bulk}$ exhibits luminescence at 720 and 820 nm, attributed to oxygen vacancies.[6]

The luminescence intensity depends on the degree of Cu^{2+} exchange in all samples, reaching its maximum unaffected by the reducing gas at about 3% copper content for Cu-4A and about 20% for Cu-13X. Very dry samples did show almost no decrease in intensity during the data collection, thus photodegradation is negligible. With small quantities of H$_2$O added (less than 1 mbar per addition) while collecting data, a strong increase in intensity occurred. After more water was added, the increase became less pronounced and eventually turned into a slight decrease. From this we conclude that there exists an optimum degree of hydration, which is quite low. Samples with water content different from this optimum show about one order of magnitude less luminescence. The intensity decrease during the measurement can be explained by the desorption of water owing to local heating of the sample caused by non-radiative deactivation of Cu$^+$.

The *in situ* experiments have allowed us to observe the differing behaviour of the Cu$^+$ zeolite emission, depending on the type of zeolite, on the reducing gas and on the water content of the samples. In the case of Cu$^+$-4A a new low energy emission band could be observed. *In situ* time-resolved spectroscopy as a sensitive probe to small changes in the environment of the emitting species will lead to a better understanding of the details of the system and will allow more precise quantification of the effect of various parameters such as the number of water molecules present.

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