24 h, then cooled to 0 °C, and quenched with aqueous hydrochloric acid (3 M, 5 mL). The resulting mixture was warmed to 23 °C and stirred for 30 min, at which point aqueous sodium hydroxide (3 M, 10 mL) was added. The mixture was stirred at 23 °C for 30 min and extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. Column chromatography on silica gel eluting with 30 % diethyl ether in pentane afforded (*R*)-2-ethyl-2-methyl-2,3-dihydrocinnamyl alcohol **5a** (239 mg, 1.34 mmol, 96 %) as a colorless oil. ^{1}H NMR ($CDCl_3$): $\delta = 7.19 - 7.31$ (m, 5H), 3.33 (s, 2H), 2.61 (AB, 2H, $J = 24.6$ Hz), 1.58 (bs, 1H), 1.27 – 1.40 (m, 2H), 0.93 (t, 3H, $J = 7.5$ Hz), 0.82 ppm (s, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 139.0$, 130.8, 128.1, 126.2, 68.4, 42.8, 39.1, 29.1, 21.0, 8.3 ppm. High-resolution FAB-MS: m/z (M+H): 179.14359 ($C_{12}H_{19}O^+$ requires 179.14359). $[\alpha]_D^{25} = -5.9$ (c = 14.2, CH_2Cl_2). The product was determined to have 94 % *ee* by HPLC (Chiralcel OD column, eluting with 1 % 2-propanol in hexanes at 0.7 mL min^{-1}; $R_t = 20.5$ min (major enantiomer), 22.8 min (minor enantiomer)).

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The Chemistry of the Oxychlorination Catalyst: an In Situ, Time-Resolved XANES Study**

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Almost all of the world production of vinyl chloride today is based on cracking of 1,2-dichloroethane. For many decades, this compound has been produced by catalytic oxychlorination of ethylene with hydrochloric acid and oxygen [Eq. (1)]. The reaction is performed at 490 – 530 K and 5 – 6 atm (1 atm ≈ 1.01×10^5 Pa) using both air and oxygen in fluid- or fixed-bed reactors.[1]

$$C_2H_4 + 2\,HCl + \tfrac{1}{2}O_2 \rightarrow C_2H_4Cl_2 + H_2O \quad (1)$$

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Commercial catalysts are produced by impregnation of γ-alumina with $CuCl_2$ (4–8 wt% Cu). Other chlorides (mainly alkali or alkaline earth metal chlorides) in variable concentration are also added to make the catalyst more suitable for industrial reactors.[1–3] In spite of an abundant literature on the subject,[1–8] a significantly improved knowledge of the system—limited to the basic catalyst (containing only $CuCl_2$ without additives)—has been achieved only recently.[4, 6–8] In particular, it has been shown by feeding separately the three reagents that the oxychlorination reaction (1) is catalyzed by a highly dispersed $CuCl_2$ phase[4, 6] and follows a three-step redox mechanism: a) chlorination of ethylene by reduction of $CuCl_2$ to CuCl [Eq. (2)], b) oxidation of CuCl to an oxychloride [Eq. (3)], and c) re-chlorination of this oxychloride with HCl [closure of the catalytic cycle,[7, 8] Eq. (4)].

$$2\,CuCl_2 + C_2H_4 \rightarrow C_2H_4Cl_2 + 2\,CuCl \quad (2)$$

$$2\,CuCl + \tfrac{1}{2}O_2 \rightarrow Cu_2OCl_2 \quad (3)$$

$$Cu_2OCl_2 + 2\,HCl \rightarrow 2\,CuCl_2 + H_2O \quad (4)$$

However, as no information is available on the true state of the catalyst in the simultaneous presence of all three reagents, it is not possible to identify the rate-determining step of the reaction. Here we report the first temperature-resolved investigation on the oxidation state and activity of the catalyst under true reaction conditions. The aim of the present work is to identify how the chemistry of the copper species controls the catalytic functions and how the presence of potassium (that is, the typical additive of fixed-bed industrial catalysts) modifies the chemical properties of the copper species and thus the catalytic behavior of the catalyst.

The temperature was increased from 373 to 623 K and then decreased again to 373 K to model the wide range of temperature that can be found in the different zones of the fixed-bed reactors at different periods of catalyst lifetime. The oxidation state of the catalyst was monitored by the shift of the Cu_K edge in XANES spectra.[9] XANES spectroscopy has been shown to be very sensitive to $Cu^I \rightleftarrows Cu^{II}$ changes,[7, 8, 10–13] and has the further advantage that X-rays are particularly suitable for in situ studies. The present study was performed on the basic catalyst (hereafter Cu5.0), and then it was extended to a catalyst containing also KCl (hereafter K3.6Cu5.0).

The $Cu^{II} \rightarrow Cu^I$ reduction can be deduced from the decrease of the white-line intensity (Figure 1a, b) and from the blue shift of the absorption edge, more evident in the first derivative spectra (Figure 1c). A comparison of these XANES spectra with those of model compounds reveals that the low-temperature spectra are close to that of $CuCl_2$, while the high-temperature ones are close to that of CuCl.[14] Quantitative information on the Cu^I and Cu^{II} concentration was obtained from the cross analysis of edge position and maximum of the first derivative spectrum.[12]

The results obtained on Cu5.0 during the complete temperature cycle are reported in Figure 2a, b. At the starting point (373 K), only Cu^{II} is present and the catalyst is inactive. O_2 conversion and Cu^{II} reduction start in the same temperature range (470–490 K) and progressively increase with temperature. Cu^{II} reduction becomes complete at 600 K. During the cooling step, the conversion progressively declines and becomes negligible in the 490–470 K range, while the oxidation state of Cu does not change. The results entail that,

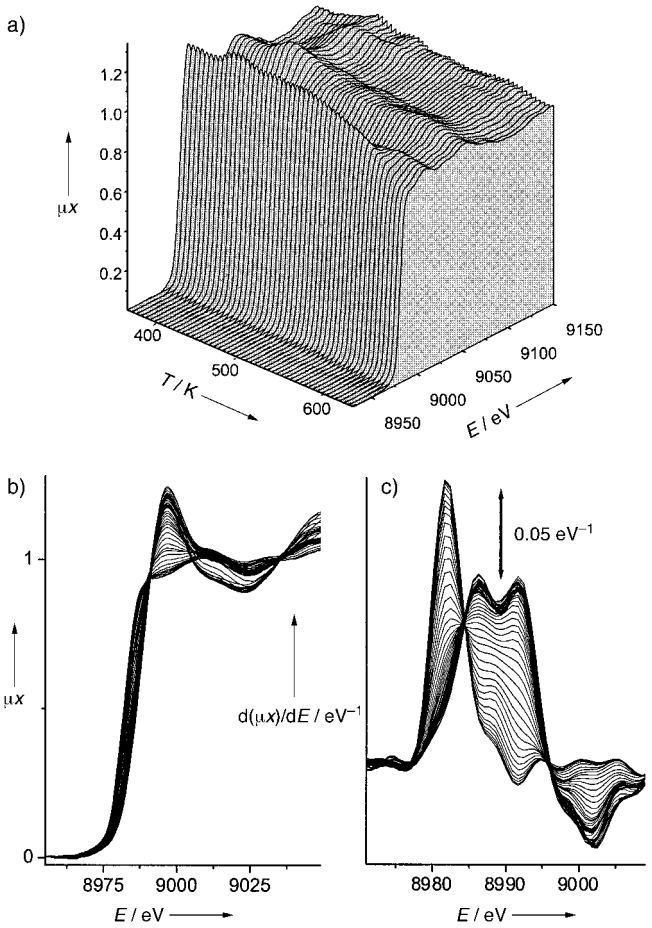

Figure 1. a) Three-dimensional XANES spectra (collected each 30 s) of Cu5.0 during heating from 373 to 623 K with 12 K min^{-1}. b) Front view of the spectra shown in (a). c) Derivative spectra, Fourier filtered to remove the high-frequency noise. E = photon energy, μx = normalized absorption, assuming $\mu x = 1$ at $E = 9035$ eV. The presence of two isosbestic points in the XANES (8990 and 9005 eV) and derivative spectra (8984 and 8995 eV) is direct proof for only two species being present on the catalyst in significant amounts: $CuCl_2$ and CuCl in mutual transformation. The oxychloride formed according to Equation (3) is not detected because the re-chlorination step is too fast.[15]

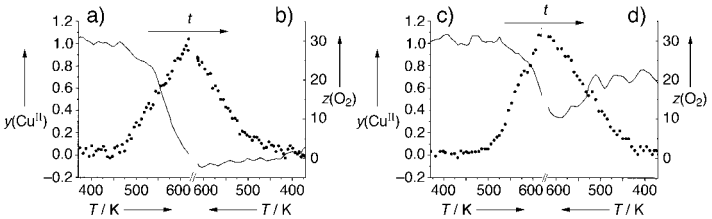

Figure 2. a) O_2 conversion (representative for the catalyst's activity; z, full dots, right axis) and Cu^{II} fraction (y, full line, left axis) for Cu5.0 during temperature ramp-up. b) As diagram (a), but for the temperature ramp-down. c) and d) Equivalent presentations to (a) and (b) for K3.6Cu5.0. The time axis runs in all diagram parts from left to right. $y(Cu^{II}) = 1 - y(Cu^I)$, where $y(Cu^I)$ has been determined by the relative intensity of the first derivative maximum at 8982 eV (Figure 1c) compared to the value obained on a totally reduced sample.

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at the typical oxychlorination temperature, Cu^{I} dominates and the rate-determining step is the oxidation of CuCl [Eq. (3)]. To understand the low efficiency of the oxidation process, the catalyst was subjected at the end of the cooling step to two different oxidizing treatments at increasing temperatures (373 – 623 K): one with diluted O_2, the other with a diluted O_2 – HCl mixture. The first treatment caused the complete Cu^{I} oxidation already at 373 K, while the second left Cu^{I} unchanged up to 550 K, and, even at 623 K, Cu^{I} was still present. This points out that HCl acts as a poison for the Cu^{I} oxidation and is responsible for the prevailing reduced state of copper during the reaction.

Figure 2c, d shows the results of the same experiment performed on K3.6Cu5.0 as catalyst. The $Cu^{II} \rightarrow Cu^{I}$ reduction began at a slightly higher temperature (around 520 K) and was not complete: 30% of Cu^{II} survived even at 623 K. The activity of this catalyst started around 490 K, that is before the reduction process. During the cooling step, Cu was re-oxidized to a fraction of 80%, and the activity survived down to 450 K.

These results indicate that addition of potassium favors the oxidized state of the catalyst, suggesting that it causes either an increase in the oxidation rate [Eq. (3)] or a decrease in the reduction rate [Eq. (2)].[15] The decrease in the reduction rate was testified by dosing ethylene alone at 500 K in a pulse reactor (see Figure in the Supporting Information) on K3.6Cu5.0 and Cu5.0 catalysts following a procedure previously reported.[6] These data imply that the rate-determining step of the oxychlorination reaction (1) catalyzed by K3.6Cu5.0 is the reduction of the active phase.

The deactivating effect of potassium cannot be attributed to a decrease in the copper chloride active surface area, because the Cu dispersion, measured by CO adsorption at room temperature (RT)[7] on samples previously reduced in H_2, is the same (Cu5.0: 47%, K3.6Cu5.0: 49%). The effect should be rather ascribed to the formation of a mixed chloride (K_xCuCl_{2+x}),[16] which reduces the ability of the active surface to adsorb ethylene and/or transfer two Cl atoms to each ethylene molecule. The formation of the mixed chloride, although not detectable by XRD owing to too small crystal size,[6] is suggested by IR spectroscopy of adsorbed CO on samples previously reduced in ethylene (Figure 3). The absorption bands are due to the formation of $Cu^{I} \cdots CO$ adducts.[7, 17] The difference in $\tilde{\nu}$(CO) (2139 cm^{-1} for Cu5.0 and 2117 cm^{-1} for K3.6Cu5.0) implies that the Cu^{I} ions on the two catalysts belong to different compounds: a totally reduced CuCl salt for sample Cu5.0[7, 17, 18] and a mixed, partially reduced potassium – copper chloride for sample K3.6Cu5.0. The lower intensity of the bands in Figure 3a reflects the lower ability of this catalyst to be reduced by ethylene, supporting the XANES data.

The moderating effect of potassium on the catalytic activity allows to control the formation of hot spots, associated with the strong exothermicity of the oxychlorination reaction. This explains why loading the industrial reactors with catalysts having a decreasing K/Cu ratio in the direction of the flow of the reactants improves performance and catalyst lifetime. Moreover, the favored oxidized state +2 of Cu minimizes the Cu loss caused by the volatility of Cu^{I} species.

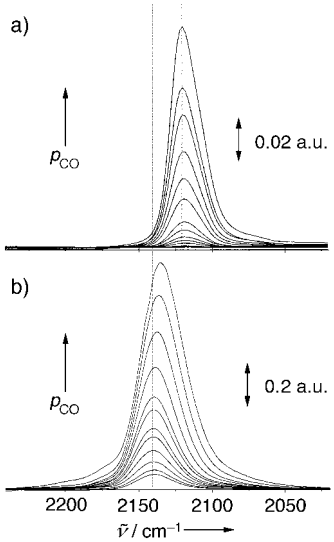

Figure 3. RT IR spectra (same scale) obtained when CO with increasing pressure p_{CO} was dosed on K3.6Cu5.0 (a) or Cu5.0 (b), previously reduced in C_2H_4 at 500 K for 1 h. a.u. = absorbance units.

In conclusions, we could identify the rate-determining step in the ethylene oxychlorination reaction catalyzed by $CuCl_2/\gamma$-Al_2O_3 and clarify and experimentally prove the role of the potassium dopant in catalysts used in fixed-bed industrial reactors: the alkali metal ion modifies the redox properties of the copper species favoring its oxidized state.

Experimental Section

The samples, containing either 5.0 wt% Cu (labeled Cu5.0) or 5.0 wt% Cu plus 3.6 wt% K (labeled K3.6Cu5.0), were prepared from chlorides following the incipient-wetness method.[4] The experiments were performed by feeding a cell containing a self-supported thin pellet of the catalyst with a diluted mixture of the three reagents(C_2H_4:HCl:O_2:N_2 = 100:36.1:7.6:180), representative of the fixed-bed process. In the course of the experiment the temperature was increased from 373 to 623 K and then decreased again to 373 K. The gas output was analyzed with a Balzer Quadstar 422 quadrupole mass spectrometer. XANES spectra were collected at the ID24 dispersive EXAFS beamline[19] of the ESRF facility. For IR measurements, performed at RT, a thin self-supporting wafer of the catalyst was prepared and activated under dynamic vacuum at 500 K for 2 h inside an IR cell designed to allow in situ temperature treatments, reagents dosage, evacuation, and CO dosage. The IR spectra were recorded at a 2 cm^{-1} resolution on a BRUKER FTIR 66 spectrometer equipped with a mercury – cadmium – telluride cryodetector.

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Comparison of Reorganization Energies for Intra- and Intermolecular Electron Transfer**

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The reorganization energy (λ), which is a sum of two terms, inner-sphere reorganization energy, λ_i, and outer-sphere reorganization energy, λ_o, imposes probably the most far-reaching impact on biological electron-transfer (ET) systems.[1] In particular, the primary ET processes in photosynthesis are all characterized by small reorganization energies.[2] This situation allows, for instance, forward ET processes to proceed under nearly optimal conditions, that is, near the top region of the Marcus parabola, whereas the highly exergonic and energy-wasting back-ET process is shifted deeply into the inverted region. To achieve small reorganization energies, it is highly desirable for the construction of artificial photosynthetic systems to employ donor – acceptor couples, which offer room for the delocalization of the charges—electrons or

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