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Electronic Supplementary Information (ESI)

Delafossite-based copper catalyst for sustainable Cl_2 production by HCl oxidation

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Catalyst preparation

$CuAlO_2$ delafossite was prepared by solid-state reaction of a physical mixture of Cu_2O (Strem, 99.9%) and γ-Al_2O_3 (Alfa Aesar, 99.997%) in air. The homogenised stoichiometric mixture, obtained by ball milling of the oxides for 30 min, was subjected to calcination at 1373 K (10 K min^{-1}) for 30 h. The resulting solid contained impurities of CuO and $CuAl_2O_4$. Single-phased delafossite was obtained by repeating the grinding and calcination steps under the same conditions. $CuAl_2O_4$, $Cu_{0.5}Al_2O_4$, and $Cu_{0.5}K_{0.1}Al_2O_4$ were synthesised by continuous co-precipitation (*Adv. Mater*. 2006, ***18***, 2436), using aqueous solutions containing the corresponding metal nitrates in the required molar ratios and a mixture of NaOH+Na_2CO_3 (1 M each) as the precipitating agent. The obtained slurries were aged at 313 K for 12 h under mechanical stirring (500 rpm), followed by filtration, washing, drying at 333 K for 12 h, and calcination at 1173 K (10 K min^{-1}) for 5 h. The supported catalyst, CuO/α-Al_2O_3 (20 wt.% Cu) was prepared by dry impregnation of the alumina carrier (Alfa Aesar, 99.98%) with an aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ (Alfa Aesar, 98.0%), followed by drying at 333 K for 12 h and calcination at 773 K (10 K min^{-1}) for 5 h. All calcinations were conducted in static air.

Catalytic testing

The oxidation of HCl with O_2 over $CuAlO_2$ was first studied in a lab-scale quartz fixed-bed micro-reactor described elsewhere (*J. Catal*. 2010, ***276***, 141), using 0.5 g of catalyst diluted with 2 g of glass spheres (Spheriglass®, diameter = 0.5-0.6 mm), a total flow of 10 l STP h^{-1}, and a total pressure of 1 bar. The catalyst was tested in the temperature range of 623-723 K using a feed mixture with 10 vol.% HCl (Messer, purity 2.8, anhydrous) and 5-90 vol.% O_2 (Pan Gas, purity 5.0), balanced in N_2 (Pan Gas, purity 5.0). These preliminary tests enabled to obtain

relevant kinetic information such as the temperature and O_2/HCl ratio dependences. The long-term stability of $CuAlO_2$, $CuAl_2O_4$, $Cu_{0.5}Al_2O_4$, $Cu_{0.5}K_{0.1}Al_2O_4$, and CuO/α-Al_2O_3 in HCl oxidation was assessed in a similar laboratory reactor at Bayer MaterialScience in Dormagen, Germany. The samples were evaluated at 1 bar and 653-703 K using an inlet O_2/HCl ratio of 2 or 4 and a total flow of 5 or 10 l STP h^{-1}. In all cases, the catalysts (sieve fraction = 0.4-0.6 mm) were diluted with glass spheres as described above. Dilution is essential in long runs due to coagulation of the catalyst bed, which often occurs with unstable Deacon catalysts. Bed coagulation causes a high pressure drop, which forces to abort the test. Blank experiments with only Spheriglass® spheres (soda-lime glass with 73% SiO_2, 14% Na_2O, and 9% CaO as the major constituents) were conducted in order to confirm the inactivity of the catalyst diluent under reaction conditions. In order to quench the reaction at selected times and unload samples for subsequent characterization, the reactor was rapidly cooled down to room temperature in inert flow. Quantitative Cl_2 analysis was carried out by iodometric titration. The gas mixture at the reactor outlet was absorbed in an aqueous KI (Sigma-Aldrich, 99%) solution (2 wt.%). The thus formed iodine was titrated with an aqueous $Na_2S_2O_3$ (Sigma-Aldrich, 98%) solution 0.01 M.

X-ray diffraction

Powder X-ray diffraction (XRD) was measured in a PANanalytical X'Pert PRO-MPD diffractometer. Data were recorded in the range 10-70° 2θ with a step size of 0.017° and a counting time of 0.26 s per step. Samples unloaded from the reactor at different times were ground prior to analysis in order to reduce the glass spheres to powder. The corresponding diffractograms are shown in Fig. S1. In the cases of the samples exposed to reaction conditions for 970 and 1200 h, diffraction lines specific to NaCl and $CaSiO_3$ were detected. These phases formed upon prolonged contact of the soda-lime glass spheres with HCl at the reaction temperature. The different intensity of their diffraction lines for the two samples might arise from the inhomogeneous nature of the mixture catalyst powder-glass spheres. Importantly, no crystalline phase involving copper with either sodium or calcium was identified, which enables to exclude undesired solid-state reactions between catalyst and diluent.

X-ray fluorescence

The chemical compositions of the samples unloaded at different times on-stream were determined by X-ray fluorescence in a Siemens Bruker SRS 3400 WDXRF spectrometer. The samples were measured in powder form.

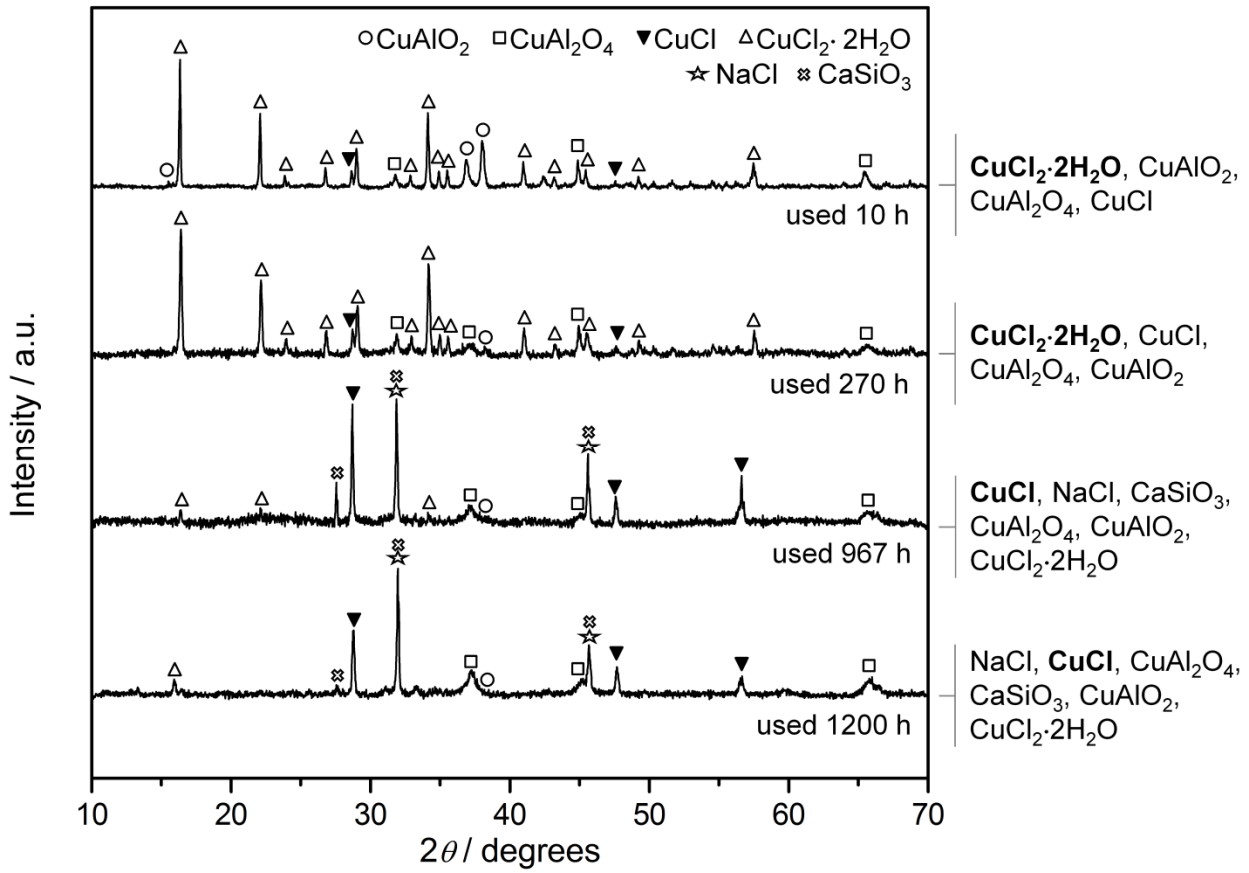

Fig. ESI1. X-ray diffraction patterns with detailed phase identification of selected samples after HCl oxidation at different times on-stream. The right panel lists the crystalline phases present in the samples, with the predominant copper phase in bold. Crystalline phases: $CuAlO_2$ (JCPDS 75-1988), $CuAl_2O_4$ (JCPDS 01-1153), CuCl (JCPDS 77-2383), $CuCl_2{\cdot}2H_2O$ (JCPDS 76-0569), NaCl (JCPDS 88-2300), and $CaSiO_3$ (JCPDS 89-4051).