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Reaction Mechanism of the Exchange Reaction between CuCl and BaO Studied by Time-Resolved X-ray Absorption Spectroscopy

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The solid state reaction $2CuCl+BaO \rightarrow Cu_2O+BaCl_2$ has been examined *in situ* using energy-dispersive X-ray absorption fine-structure spectroscopy (DXAFS). A high time resolution on the order of seconds between two Cu K-XANES spectra has been achieved by this experimental setup. The spectra suggest that the transformation of CuCl to Cu_2O is preceded by an unidentified, intermediate state. Fingerprint methods as well as principal component analysis have been applied, which confirm the formation of exactly one new intermediate phase. The nature of this phase remains unidentified and could not be elucidated by the experimental investigations. © 2002 Elsevier Science

Key Words: **XANES; time resolved; XAFS; Hedvall reaction; CuCl; BaO.**

INTRODUCTION

Regarding the historical development of solid state chemistry, J. Arvid Hedvall is definitely considered one of the pioneers who have worked on this matter. In the 1920s he studied a class of reactions between solids, basically between oxides and salts, often called exchange or Hedvall reactions (1). Hedvall's work mainly consists of analyzing exothermic curves in heating diagrams of these reactions, a method commonly known as differential scanning calorimetry (DSC). One of his major goals was the identification of intermediate products. However, the experimental tools in those decades were not well suited to identify short-lived reaction intermediates in solid phases.

In recent years, some effort has been spent on elucidating this former question. Particularly one type of Hedvall reaction (2), which takes place between oxides and oxysalts, has been studied intensively. García-Clavel *et al.* (3) analyzed the reaction $CuSO_4 + PbO \rightarrow CuO + PbSO_4$ by thermoanalytical and mass spectrometrical means. They proposed the formation of SO_3 and remarked that the phase of PbO seems to be important for the reaction path. Arnold *et al.* (4) used *in situ* X-ray diffraction to analyze the reaction $CuSO_4 + BaO \rightarrow CuO + BaSO_4$ and they assumed crystalline oxysulfates as reaction intermediates. However, amorphous intermediates are not detectable by X-ray diffraction (XRD), and it seems reasonable that short-lived intermediates might not crystallize fast enough to be found by this method.

X-ray absorption fine-structure spectroscopy (XAFS), however, has the potential to detect the local environment of probed atoms that are part of an amorphous structure (5). In recent work, time-resolved X-ray absorption near-edge structure (XANES) spectroscopy proved efficient to identify the reaction mechanism during the thermal decomposition of ammonium hexachlorometallates of noble metals ($(NH_4)_x[MCl_6]$) (6, 7). These results exceeded the information detectable by thermal analysis and temperature-dependent XRD. It was possible to determine reaction temperatures and to identify intermediate states during the solid state reactions.

In this work, we present results concerning reaction mechanism and intermediate states of the Hedvall reaction (8) $2CuCl + BaO \rightarrow Cu_2O + BaCl_2$ by means of dispersive XAFS (DXAFS) (9).

EXPERIMENTAL

Cu *K*-XANES spectra have been measured at the Bonn electron storage ring ELSA (10). The ring parameters were 2.3-GeV electron energy at an average current of 40 mA. The Lemonnier-type double-crystal monochromator (DCM) at beamline BN3 (11) equipped with Ge⟨422⟩ crystals has been used to measure XANES spectra of reference compounds (CuCl, Cu_2O) obtained by Aldrich as well as copper foil. The detection mode was transmission, measured by means of ionization chambers placed in front of and behind the sample. Data analysis was performed by subtracting a linear background and rescaling the absorbance by

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normalizing the difference between the baseline and the absorption approximately 150 eV behind the edge to one. The first inflection point of the Cu metal foil was the reference point for energy calibration (8979 eV). With a series of Cu foil XANES spectra, the reproducibility was shown to be better than ± 0.2 eV.

Time-resolved spectra were obtained with the energy-dispersive monochromator (EDM) at beamline BN1 (9). A principal time resolution of up to 4 ms/spectrum is possible by using a bent Si⟨400⟩ crystal as a monochromator. The relation between beam position on the curved crystal and Bragg angle is linear in a first-order consideration, thus allowing the reflection of the complete energy range, which is necessary for a XANES spectrum. The energy is encoded within the horizontal reflection angle. Since the polychromatic reflection is focused on the sample, it is possible to collect a complete XANES spectrum in one "shot" by means of a position-sensitive detector. This is realized by a linear 1024 pixel photodiode array (Reticon RL1024SAU-011). The specific integration time per spectrum was 860 ms to maximize the detection signal, which was weak due to high absorption in the sample. To improve the signal-to-noise-ratio, an averaging of 12 scans was carried out, which led to a total read-out time for a single XANES scan of 12 s, including the time for data processing and communication.

Again, to compare the measured absorption curves quantitatively, a linear background was fitted to the pre-edge region (8955–8970 eV) and subtracted from the complete spectrum before normalizing with respect to the edge jump, which has been determined as the average value of the first EXAFS oscillations. Finally, the energy-dispersive spectra were slightly filtered by calculating the average value between three neighboring photodiode pixels. This smoothing does not affect the spectral resolution, which has been estimated to be 1.5 eV since the small distance between two detector pixels would allow an energetical resolution of 0.19 eV in the applied geometry of 1080-mm distance between sample and virtual center of the cylindrically bent crystal.

For the *in situ* measurement, a water-cooled heating cell was used to control the temperature on the sample. A homogeneous mixture of BaO (55 wt %) and CuCl (45 wt %) was prepared to obtain a stoichiometry of BaO:CuCl = 1:1. The powders were filtered to obtain an upper limit of 50 μm for the grain size to favor the diffusion process since diffusion on the grain border starts at lower temperatures. Fifteen milligrams of the powder was spread homogeneously on the surface of a thin glass-fiber plate consisting mainly of SiO_2, which is temperature resistent up to about 850°C. A low nitrogen flow (ca. 0.1 ml/s) was set to reproduce the experimental conditions of J. A. Hedvall (8). The construction of the heating cell forces the nitrogen gas (99.99 vol%) to penetrate through the sample before leaving the reaction chamber, meaning that all volatiles are removed from the sample by the permanent gas flow. Due to the minor overpressure generated by the gas flow, no oxygen or air can enter the heating cell and reach the sample during the thermal reaction.

A Ni–Cr/Ni thermocouple was fixed near the sample holder to feed the temperature controller. This setup supported a linear temperature ramp of 9 K/min, resulting in a temperature increase of 1.8°C between two spectra. Knowing that SiO_2 is a bad heat conductor, we tested the temperature by fixing temperature control strips on the center of the glass-fiber plates in a test run and corrected the measured temperature data for this effect.

RESULTS

A selection of time-resolved Cu *K*-XANES spectra of the exchange reaction is shown in Fig. 1. The numbers 1–5 and the five vertical dotted lines refer to interesting structures, indicating small changes of the absorption coeffecient, which will be specified later. Between 256 and 390°C, every tenth spectrum is included in the graph in addition to the spectrum of 25°C and two reference spectra of CuCl and Cu_2O. Considering the energy-dispersive spectrum at

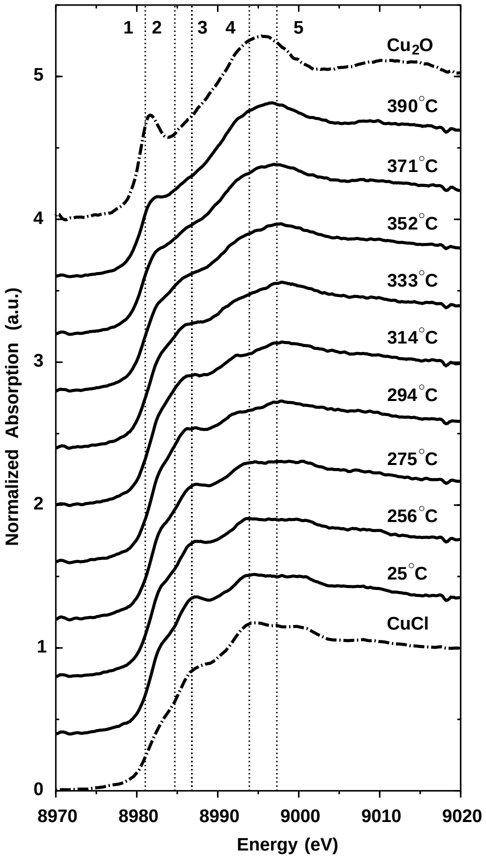

FIG. 1. Time-resolved Cu *K*-XANES measurements of $2CuCl + BaO \rightarrow Cu_2O + BaCl_2$ recorded at the EDM.

390°C, general agreement with the Cu K-XANES spectrum of Cu_2O is obvious. The same accordance can be found regarding the Cu K-XANES of CuCl and the spectrum at room temperature (25°C). Therefore, we can conclude that the expected reaction $2CuCl + BaO \rightarrow Cu_2O + BaCl_2$ does take place. The mismatch between reference spectra and DXAFS XANES can be explained by the thickness effect, which becomes manifest by the enhanced near-edge features relative to the edge height as well as very low post-edge features (12) and a slightly different experimental resolution between the DCM and DXAFS monochromator.

Due to the large amount of data, it is not possible to discuss every spectrum in detail and it seems more efficient to reduce the most important features of the XANES spectra to one value. Particularly, the edge position and shape as well as pre-edge features are interesting since two important effects are encoded in this part of the spectrum. The position of the edge, usually determined by the first inflection point of the spectrum, is a strong indicator for the valence state of the probed atom. In copper oxides, an inflection point at 8980.5 eV corresponds to a monovalent copper oxide whereas 8984 eV corresponds to a divalent compound. But there is no exact linear relation between valence state and energy position of the inflection point since electronegativity, atomic radii of the ligands, and other effects play an important role in the matter (13). The analysis of the time-resolved XANES concerning the inflection point does not give any significant evidence of a rising valence during the *in situ* reaction.

The second important effect in the edge jump region is the shape of the pre-edge, respectively, shoulder peak. Particularly in the XANES of 3d transition metals, the local surrounding of the probed atom manifests itself in the shape and position of these peaks (14, 15). A very efficient method of investigating small changes in the edge jump region is the integration method published by Capehart *et al.* (16). In this approach, the initial spectrum at 25°C defines the reference energy E_0 of the time-resolved series. The value of E_0 is determined as the upper limit of an integral over the edge jump, which is defined by the normalized absorption, reaching the value 1 for the first time.

A second spectrum does have a different upper limit value E for the integral, which contains the same area as the reference integral. The characteristic energy shift $\Delta E_J = E - E_0$ is shown in Fig. 2. It is possible not only to confirm Hedvall's reaction temperature (8) but also to identify the existence of a reaction intermediate in the temperature interval between 275 and 300°C according to the negative energy shift value of -0.2 eV. The negative shift is an indicator for the valence state of the intermediate, which contains most probably a mono- or zerovalent copper atom. This can be assumed since the shift of the spectrum to higher energies results from a chemical reason; namely, the increased bonding energy of the K-shell electron if the atomic core is positive compared to the zerovalent metal (13).

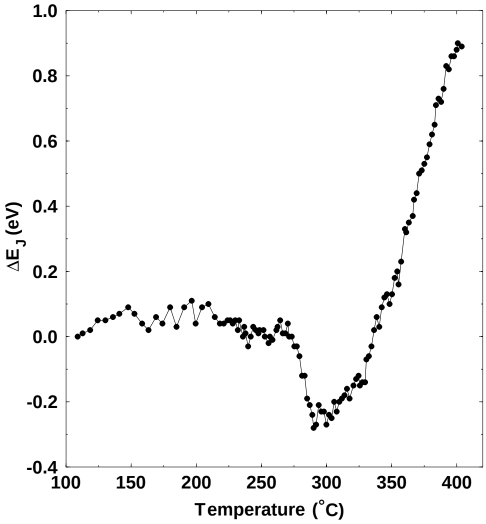

FIG. 2. The characteristic energy shift ΔE_J determined by integration over the Cu K-edge jump during the reaction $2CuCl + BaO \rightarrow Cu_2O + BaCl_2$.

The differences between several selected spectra and the initial 25°C XANES spectrum are shown in Fig. 3. Features 2 and 4 at 8984.5 and 8994 eV show that an intermediate state emerges in the specified temperature region since the changes in relation to the initial XANES spectrum disappear again at higher temperatures and are replaced by peaks 1 (8981 eV), 3 (8987 eV), and 5 (8997.2 eV). However, nonlinear distortions of the near-edge spectra, which can be caused by the thickness effect (12), might affect the analysis of the

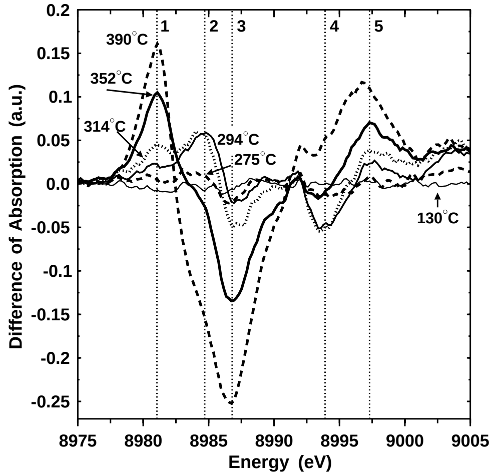

FIG. 3. Cu K-XANES difference spectra relative to the first spectrum of the time-resolved XANES series $2CuCl + BaO \rightarrow Cu_2O + BaCl_2$.

difference spectra. To support the result, a second method of investigation has been applied.

The number of base states that contribute to a time-resolved series of XANES spectra can be calculated by principal component analysis, as shown by Wasserman (17). For this purpose, the entire data set is written into one matrix, which is decomposed into eigenvectors using the singular value decomposition technique (18). These abstract eigenvectors (called factors) are sorted by their eigenvalues, which correspond to their weight. For this method it is not necessary to know the physical eigenvectors or base states. To determine the number of factors needed, reconstructing the data matrix by a matrix of linear combinations of one to eight eigenvectors is attempted.

The number of base states, and therefore the number of intermediate states, can be concluded from three parameters. First, the eigenvalues or weights of all factors beyond the required ones should be similar and comparatively small. In Fig. 4a the eigenvalues decrease below a significant value from factor four onward. Second, if more factors than necessary are used in reconstruction, the real error is not reduced any further. In Fig. 4b the real error reaches a minimum when three factors are used. Third, the imbedded error decreases with the number of factors used until a minimum is reached at three factors (Fig. 4c). All further factors represent noise and increase the imbedded error. We can conclude that each of the 140 XANES spectra is a linear combination of exactly three base spectra, of which two are the known initial and final states and one is the intermediate state.

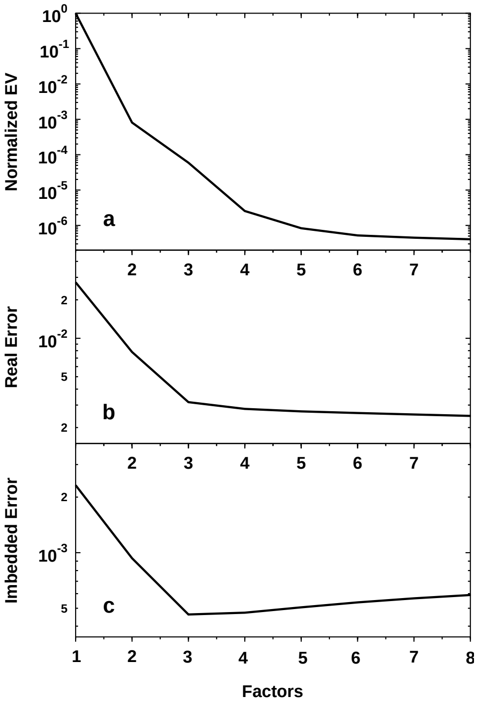

FIG. 4. Factor analysis results of the time-resolved XANES spectra: (a) normalized eigenvalues (EV), (b) real error, and (c) imbedded error. Dotted lines are added to guide the eye.

DISCUSSION

There are usually two different approaches of analyzing XAFS spectra that could reveal information about the nature of the reaction intermediate and enable a better understanding of the reaction mechanism. Primarily, it is possible to investigate the extended X-ray absorption fine structure (EXAFS) that probes the radial distribution and distance of nearest neighbored backscatterers surrounding the aborbing atom. The second method is to compare XANES spectra of known reference compounds by the fingerprint method.

First, experiments to analyze the EXAFS structure have been carried out using the DXAFS spectrometer but it was not possible to collect acceptable Cu *K*-edge data within these trials. The reason for this failure is based on the bending mechanism of the monochromator crystal, which does involve a geometrical aberration at the polychromatic focus point and results into artefacts due to the inhomogeneous sample thickness (19). Moreover, the amount of the intermediate phase in the CuCl/BaO matrix is very small. There might be a chance in subtracting the EXAFS signal of CuCl from the spectrum that contains the intermediate state but the influence of the Debye–Waller factor has to be taken into account. Finally, it is no easy task to separate the different contributions of light elements such as chlorine and oxygen backscatterers. Despite this troublesome dataanalysis, the idea persists to stop the reaction at an intermediate stage and to take full EXAFS scans of the sample after cooling it down to room temperature. Although this is not an *in situ* approach, some effort has been made using a conventional double-crystal monochromator, but it was not possible to stop the reaction in a controlled manner and to isolate the intermediate phase. In conclusion, the *in situ* EXAFS analysis does not seem to be an appropriate method for investigating diffusion-controlled solid state reactions such as Hedvall reactions.

Second, some effort has been spent to obtain information about the reaction mechanism by the analysis of characteristic XANES structures using the above-mentioned fingerprint method. Regarding the phase diagram of Cu–O in Fig. 5, no copper oxide can be found that might be a candidate for the intermediate state. Further on, the melting point of the copper oxides is very high, exceeding 1000°C. However, the melting temperature of CuCl turns out to be only 422°C. Although this is far above the formation temperature of the intermediate phase at 275°C, it seems possible that the crystal lattice of CuCl begins to deform at even lower temperatures. To indicate a possible involvement of the

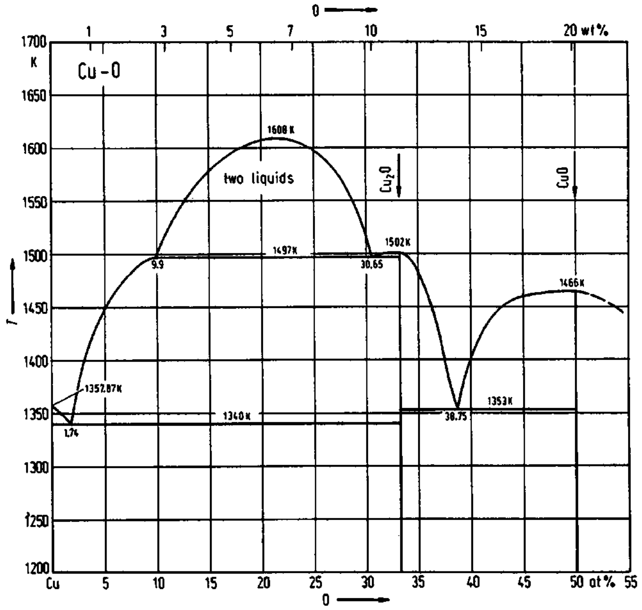

FIG. 5. Cu–O. Phase diagram (0...55 at.% O) taken from (20).

melting process during the formation of the intermediate state, it might be useful to take XANES spectra of CuCl *in situ* when approaching this temperature. Since the melting temperature of CuCl is very low compared to the melting point of BaO (1973°C), it seems reasonable to assume that the disproportionation of copper chloride is the first step in the exchange reaction. A conceivable reaction path is expressed by the equation $2CuCl \rightarrow Cu + CuCl_2$. Regarding the energy shift in Fig. 2, which is correlated with a corresponding negative valence shift, it is convincing to suggest a mechanism that involves the formation of zerovalent "metallic" copper. The shape of the near-edge resonances might be modified by the increased influence of the thickness effect due to the involved diffusion process that reduces the homogenity of the sample. Therefore, the investigation of the energy shift should not be overestimated.

Moreover, the linear combination of the crystalline reference spectra of Cu and $CuCl_2$ does not resemble the spectrum of the intermediate state. The same maladjustment was found when including a set of additional reference spectra, namely, crystalline CuO, Cu_2O, CuCl, and Cu_2Cl_2O, into the linear combination. Due to the lack of reasonable reaction intermediates, it might be arguable that reference spectra of crystalline compounds can be used to reconstruct the *in situ* spectra of the intermediate state. Frequently, so-called "X-ray amorphous" phases reveal a nanocrystalline structure that cannot be distinguished from crystalline samples regarding the X-ray absorption spectrum. The reason is that the short-range order that characterizes the X-ray absorption spectrum remains usually unharmed in nanocrystals. Nevertheless, "true" amorphous samples or liquids certainly show a different XANES structure. Therefore, it cannot be ruled out that amorphous phases play an important role. Finally, it seems conceivable that the intermediate state might be an amorphous form of Cu_2O or of CuO as well as a mixture of Cu/Cu–oxides. The latter is commonly observed in heterogeneous catalysts containing Cu in contact with, e.g., ZnO (21).

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