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SEM–EDX and SAM–AES Investigations on Rochow Contact Masses

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Appropriate Rochow contact masses have been investigated by the spatial resolution techniques SEM–EDX and SAM–AES. The results gave evidence of the existence and the catalytic action of (X-ray)-amorphous copper–silicon (Cu–Si) surface species, i.e. extremely highly dispersed particles or two-dimensional species. The well-known Rochow promoter zinc seems to act as a moderator rather than as a real accelerator. It ensures a stable rate for the reaction by neutralizing the detrimental action of silicon impurities. The silicon impurities make the whole of the silicon surface reactive and in this way cause a general blockade of the silicon surface by inactive copper species. Zinc localizes the reaction. The silicon surface remains partly free, and active Cu–Si surface species can be formed by lateral diffusion of copper onto the silicon surface that is still free. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

$$Si_{powder} + CH_3Cl_{gas} \xrightarrow{\text{Cu catalyst}} (CH_3)_xH_ySiCl_z;\quad x+y+z=4 \qquad [1]$$

In the Rochow reaction (Eqn [1]), a mechanical mixture of silicon, a copper component and promoters, called the ‘contact mass’, reacts with methyl chloride in fluid-bed reactors. The reaction products, especially the main product dimethyldichlorosilane (DDS; $x=2$, $y=0$, $z=2$), are the raw materials for the whole of the silicone industry.

Although it has been realized industrially for decades, the Rochow reaction has been poorly understood. The catalytically active species within the contact mass system and the reaction mechanism are still controversial, despite the publication of numerous relevant papers (see e.g. Ref. 1–3). This situation, which is more unsatisfactory than in the case of other catalytic systems, may be due to the high complexity of the contact mass system, which contains several solids and, moreover, solid silicon as a reactant, as well as to the poor accessibility of the system to analytical methods. There has not been a real breakthrough in the selective characterization of the active surface of contact masses by typical catalyst methods such as chemisorption/thermodesorption or by modern surface methods. As a consequence, only a little is known about the detailed nature and the number of catalytically active sites.

As far as the application of surface science methods to the Rochow system is concerned, one is confronted with special problems. The method chosen must be able to differentiate between several copper species, differing in the physical and chemical state, and it must be very sensitive, because only a rather low proportion of the total copper content of the contact mass seems to be catalytically active.[4] Moreover, a high spatial resolution power is required, because the catalytic activity seems to be restricted to distinct micrometer-sized areas on the silicon surface. Several authors have applied modern surface methods to surfaces of massive silicon or massive copper silicides,[5–9] which were expected to model the surface of real powder-like contact masses. However, it is not always certain whether or not such specimens really simulate the respective properties of a real contact mass.

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So far, there have been only a few papers which have applied surface science methods to real contact masses.[10–12]

In this paper, we would like to contribute to the solution of some open questions in the field of Rochow synthesis, by investigating real powder-like contact masses using spatial resolution methods. The following two problems are concerned:

(1) The nature of the active copper species in Rochow contact masses. Here, we will refer to our recent paper.[4]

(2) The mode of action of promoters, in particular zinc.

These two topics will be introduced in the respective parts of the Discussion section.

EXPERIMENTAL

Copper component

As copper component (‘catalyst’) for preparing contact masses, anhydrous copper(II) chloride ($CuCl_2$; Merck, Germany) has been used. The original copper content in the contact masses was 5.0 wt%.

Silicon

A technical-grade silicon, Si_{tech} (Silgrain, Elkem, Norway; impurities: 0.20 wt%Al, 0.13 wt% Fe, 0.03 wt% Ca, 0.015 wt% Ti, <20 ppm V, Cr, Mn, Ni, P), and a polycrystalline silicon of semiconductor quality, Si_{pure} (Wacker-Chemie, Germany), were used. The particle size ranges of the two silicon types were from 71 to 250 μm, with the size distributions within this range being practically equivalent.

Promoter

As a promoter, pure metallic zinc powder (ECKA AS 011, >99.5% Zn) has been used, with a standardized concentration of 0.5±0.01 wt% Zn in the contact masses.

Methyl chloride

The methyl chloride used was a product with a CH_3Cl content of >99.6%. It was dried with zeolite 4-A.

Catalytic experiments

Catalytic measurements at normal pressure were carried out in a glass microreactor with a volume of 50 cm^3, described previously.[13] The reactor was shaken (rotating vibration) at 25 s^{-1}, causing an intensive whirling of the contact mass particles. Generally it was charged with 10 g contact mass. The arbitrarily chosen reaction temperature for comparing catalytic performances was 340 °C. The contact mass types $CuCl_2/Si_{pure}$, $CuCl_2/Si_{tech}$ and $CuCl_2/Si_{tech}/Zn$ were prepared by mechanical mixing of silicon powder, copper component and, if applied, zinc promoter. In order to start the synthesis reaction, the contact mass samples were dried *in situ* and afterwards heated to 340 °C in a stream of methyl chloride. The methyl chloride flow amounted to 2.7 l h^{-1}. The reaction products were analyzed by on-line gas chromatography over 15 min. The errors in reaction rates have been less than ±15%.

The methyl chloride conversion was calculated according to the literature.[14] Total reaction rates r, as a measure of the catalytic activity of the contact masses, were calculated according to $r = Fx/W$ ($F = CH_3Cl$ flow rate, $x = CH_3Cl$ conversion, W = contact mass weight). Because the DDS selectivities in all experiments of this paper were >75%, selectivities and their differences are not reported or discussed.

SEM–EDX analysis

The morphology as well as the elemental composition and distribution on the contact mass surfaces were investigated by scanning electron microscopy (SEM; Cambridge Instruments S 360) combined with energy-dispersive X-ray (EDX) spectroscopy using a Delta Class Analyzer 8000 (Kevex). The amounts of the elements silicon, copper, zinc, chlorine and oxygen were determined from their characteristic X-ray peaks. The SEM micrography was carried out with a beam energy of 15 kV and a magnification from ×1000 to ×5000. The lateral resolving power of EDX point analysis was about 2 μm.

Specimens of the reacted contact mass samples were transferred into the microscope immediately after the catalytic experiments. Due to the air contact, a small percentage of oxygen, increasing to about 5% after 24 h, was detectable on the copper-containing regions of the surface. These low quantities do not affect the conclusions drawn from the results. The SEM images did not visibly change even after weeks of air contact.

The SEM micrographs and EDX point analyses shown here are examples, selected from numerous experiments. They represent the most typical observations on the respective contact mass.

SAM–AES analysis

In order to confirm qualitatively the SEM–EDX result with the especially interesting 20 min sample of $CuCl_2/Si_{tech}/Zn$ (see below), we applied scanning Auger microscopy (SAM) combined with Auger electron spectroscopy (AES; Microlab 310F, VG Scientific) as a method with still higher resolution power than SEM–EDX. The analysis conditions were the following: beam energy 10 kV, lateral resolution about 30 nm, magnification ×4000, acquisition time 1 s/1 eV step. For detecting copper, the Auger Cu LMM triplet at 920, 849 and 776 eV has been considered.[15] The detection limit of copper was estimated to be about 2%.

RESULTS

Activity versus time dependence on the contact masses investigated

Figure 1 depicts the catalytic activity at 340 °C as a function of the reaction time of the samples investigated. Whereas in the case of $CuCl_2/Si_{pure}$ (curve a) and $CuCl_2/Si_{tech}/Zn$ (curve c) the reaction rate becomes stable after an induction period, in the case of $CuCl_2/Si_{tech}$ (curve b) the reaction rate passes through a sharp and high maximum after the induction period and reaches only a low stationary level after a steep decline. The following sections relate to these activity vs time curves.

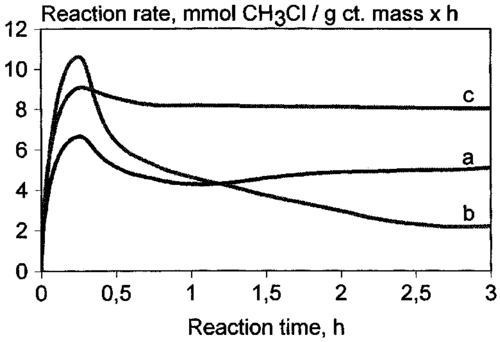

Figure 1 CH_3Cl consumption rates versus reaction time on the contact masses (a) $CuCl_2/Si_{pure}$, (b) $CuCl_2/Si_{tech}$ and (c) $CuCl_2/Si_{tech}/Zn$ at 340 °C.

$CuCl_2/Si_{pure}$

Figure 2 shows an SEM image of the $CuCl_2/Si_{pure}$ sample after 3 h reaction at 340 °C. At this time, the reaction had reached the stationary reaction rate of *ca* 5 mmol g^{-1} h^{-1} (Fig. 1, curve a). The picture allows us to distinguish (i) the silicon surface, obviously still not attacked by the reaction (e.g. point 1), with an EDX silicon surface concentration of *ca* 98%, and only traces of other elements; and (ii) reactive areas ('pits') with well-defined shapes, which have certainly been formed by attack by the silicon-consuming reaction (e.g. point 2). This corresponds to the observations of other authors in the case of real contact masses (e.g. Refs 11, 12) and also in the case of silicon model surfaces (e.g. Ref. 9).

The bottoms of the pits are structured: bright particles are to be observed there. These should contain copper, which is the heaviest element in this contact mass system. This has been confirmed by EDX point analyses, which gave copper concentrations between 10 and 30% at the bottoms of the pits. The small bright particles could not be resolved by EDX. In our preceding paper[4] we were able to show by XRD that, in all $CuCl_2$-containing contact masses, practically all of the copper added exists as the Cu–Si phase η-Cu_3Si. Hence, the bottoms of the pits are partially covered by η-Cu_3Si particles, as has already been observed or discussed by others.[9,11]

$CuCl_2/Si_{tech}$

The $CuCl_2/Si_{tech}$ sample differs from $CuCl_2/Si_{pure}$ in composition only by the silicon purity, i.e. it contains the impurities of technical-grade silicon.

As shown in Fig. 1, curve b, the steady-state reaction rate for this sample is only less than half that of $CuCl_2/Si_{pure}$. Moreover, the time course of the activities of the two samples differs strongly. Whereas the activity of $CuCl_2/Si_{pure}$ reaches a stationary position at a medium level after 1.5 h, for a short time after induction $CuCl_2/Si_{tech}$ exhibits a very high activity, which declines steeply afterwards and reaches a low stationary level after 2.5 h.

Figure 3 depicts the surface of $CuCl_2/Si_{tech}$

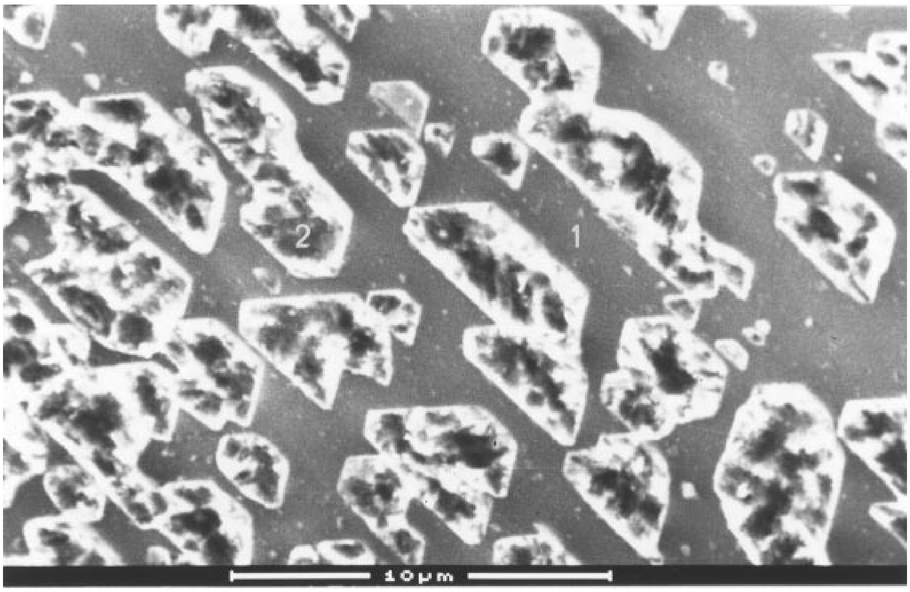

Figure 2 Scanning electron micrograph of $CuCl_2/Si_{pure}$ contact mass after 3 h reaction with CH_3Cl at 340 °C, magnification ×5000. EDX results of the non-reacted silicon surface (point 1): <0.5% Cu and 98% Si; and of a reactive area ('pit') with bright particles (point 2): 23% Cu and 73% Si.

after 3 h. The surface morphology differs strongly from $CuCl_2/Si_{pure}$. There are only a few, relatively small, 'free' silicon surface areas (e.g. point 1). The major part of the surface has obviously been attacked by the reaction and is covered with copper species of high EDX copper concentration (50–80% Cu); e.g. see point 2.

$CuCl_2/Si_{tech}/Zn$

With this zinc-promoted contact mass on the basis of technical-grade silicon, the reaction rate had already reached a high stationary level after *ca* 15 min and remained nearly constant for several hours afterwards (Fig. 1, curve c).

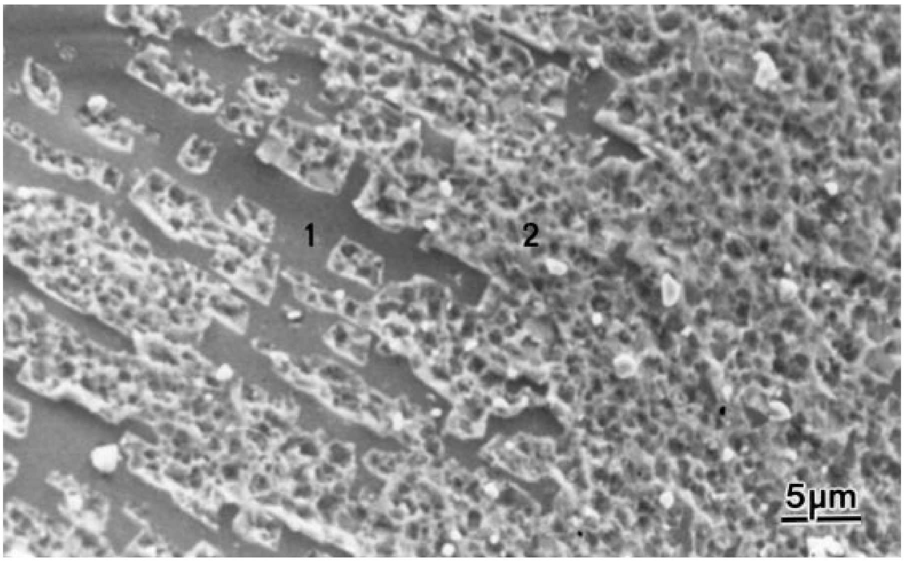

Figure 3 Scanning electron micrograph of $CuCl_2/Si_{tech}$ contact mass after 3 h reaction with CH_3Cl at 340 °C, magnification ×2000. EDX results of the non-reacted silicon surface (point 1): 0.5% Cu and 99% Si; and of the reacted surface, covered by copper species (point 2): 74% Cu and 22% Si.

Figures 4 and 5 show the surface of $CuCl_2$/Si_{tech}/Zn after 3 h and 20 min reaction time, respectively. Figure 4 is similar to Fig. 2 ($CuCl_2$/Si_{pure}), but differs from Fig. 3 ($CuCl_2$/Si_{tech}). Separate hollow-like reactive areas can be seen. At the bottoms of these pits, bright particles are

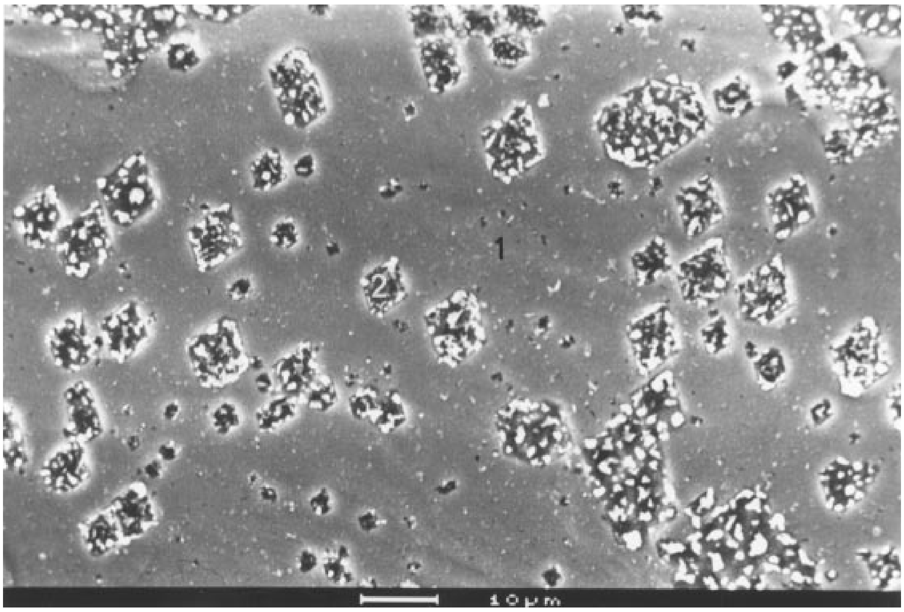

Figure 4 Scanning electron micrograph of $CuCl_2$/Si_{tech}/Zn contact mass after 3 h reaction with CH_3Cl at 340 °C, magnification ×1000. EDX results of the non-reacted silicon surface (point 1): 0.5% Cu and 98% Si; and of a reactive area ('pit') with bright particles (point 2): 15% Cu and 68% Si.

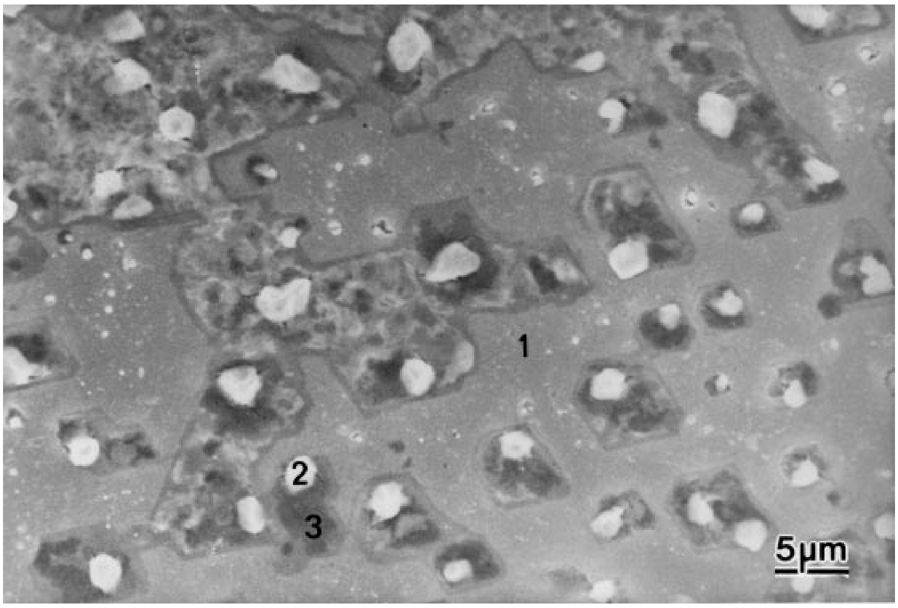

Figure 5 Scanning electron micrograph of $CuCl_2$/Si_{tech}/Zn contact mass after 20 min reaction with CH_3Cl at 340 °C, magnification ×2000. EDX results of the non-reacted silicon surface (point 1): <0.5% Cu and 96% Si; of a large grain within a reactive area (point 2): 52% Cu and 41% Si; and of an area around the grain within the pit (point 3): 2% Cu and 90% Si.

observed. The results of the EDX analyses of such pits in Fig. 4 gave copper concentrations between 10 and 30%, similar to the $CuCl_2/Si_{pure}$ sample. Here, also copper is the only heavy element, occurring in this contact mass at a considerable concentration, and, as mentioned above, all of this copper is present as η-Cu_3Si. Consequently, the bright particles should consist of η-Cu_3Si. However, as in the case of $CuCl_2/Si_{pure}$, the resolution of the EDX method was not sufficient to distinguish these small grains and the interspaces between them.

Figure 5 shows the $CuCl_2/Si_{tech}/Zn$ contact mass after only 20 min. This sample exhibited nearly the same catalytic activity as the 1 h sample; see Fig. 1. The SEM image differs from Fig. 4, however, by the large dimensions of the copper-containing particles within the reactive areas. Each pit contains only one large grain. Because of this clear arrangement, it was possible to analyze the bright particles (point 2) and their dark environment within the pits (point 3) separately by EDX. Typical analyses of the particles yielded copper concentrations around 50% and silicon concentrations around 40%. This result does not exactly correspond to the stoichiometry of η-Cu_3Si, which is certainly the substance of the particles, according to the X-ray analysis. This might be due to some excitation of the vicinity of the copper-rich particles within the pits. The key observation was that the EDX analysis of the dark areas around the grains within the holes (point 3) yielded copper concentrations of only 0.5–2% Cu, i.e. only a little higher than those on the non-attacked silicon surface. This means that in places where silicon had been consumed by the reaction, only very low amounts of copper were present.

The SEM–EDX results for the 20 min sample of $CuCl_2/Si_{tech}/Zn$ are qualitatively fully confirmed by the high-resolution SAM–AES investigation of the same sample. Figure 6 shows the SAM image and Fig. 7 the AES spectra of selected places, with the Cu (LMM) triplet between 776 and 920 eV being the indicator of copper presence. The results show that this triplet can only be observed at point 1 in Fig. 6, positioned at a large copper-containing particle within a reactive pit (see curve 1 in Fig. 7). At all other characteristic points in Fig. 6 (point 2, range beside the copper-containing particle within the same reactive area; point 5, reactive area without a copper-containing particle; point 6, non-attacked silicon area), no copper could be detected. In accordance with the SEM–EDX results this means that the copper concentration

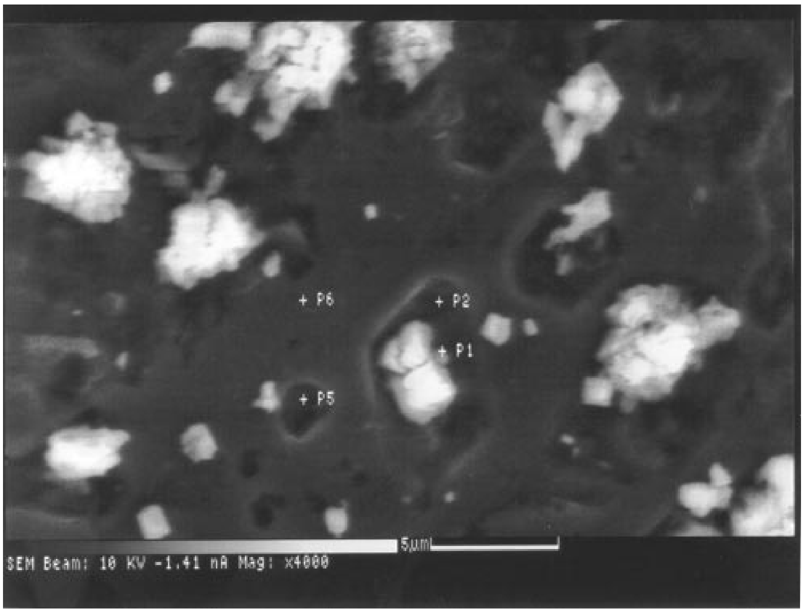

Figure 6 Scanning Auger micrograph of $CuCl_2/Si_{tech}/Zn$ contact mass after 20 min reaction with CH_3Cl at 340 °C, magnification ×4000. AES analysis points: a copper-containing grain within the reactive area, point 1; dark area beside the grain within the reactive area, point 2; a reactive area without a copper-containing grain, point 5; and non-reacted silicon surface, point 6.

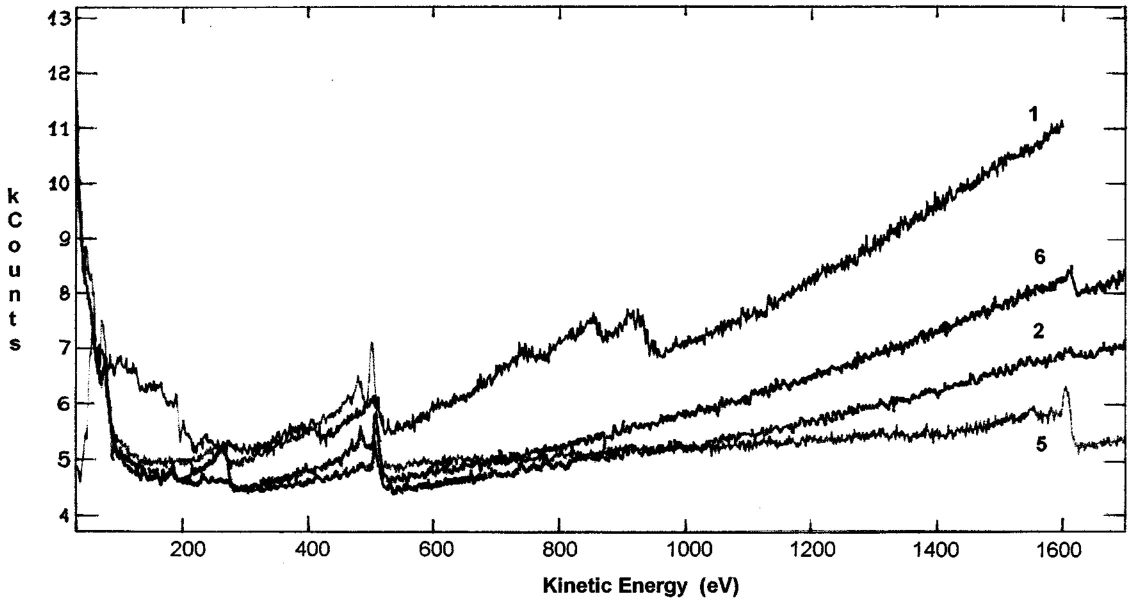

Figure 7 Auger electron spectra of the points 1, 2, 5 and 6 in Fig. 6.

has been below the detection limit of about 2 wt %. Especially, in the reactive neighbourhood of the copper-rich particles within the reactive areas, e.g. point 2, no copper has been found. Not even in the pit around point 5 was copper detectable. This pit represents a reactive area without any visible copper-containing particles.

DISCUSSION

On the nature of the catalytically active species

The nature of the active species in Rochow contact masses is still under discussion. Frequently, the η-phase Cu_3Si has been considered as catalytically active,[1–3,16] but there have also been opposing views.[17,18] In a recent paper in this journal[4] we briefly reviewed relevant papers, and we reflected on the η-phase hypothesis on the basis of catalytic and X-ray experiments on various contact masses. We concluded that the presence of η-Cu_3Si is neither a sufficient nor a necessary precondition of the Rochow reaction, and that η-Cu_3Si, if potentially active at all, needs appropriate modification in order to become active. As an alternative to the Cu_3Si hypothesis, we assumed the catalytic action of (X-ray)-amorphous Cu–Si surface species, i.e. extremely highly dispersed particles or even two-dimensional species such as Cu–Si surface compounds. Similar ideas had already been discussed speculatively a long time ago,[19] and also in a more recent paper.[20] We could explain our results consistently on this basis and by plausible arguments. More direct evidence was not available at that time.

The SEM–EDX results depicted in Fig. 5 give more direct evidence of the kind required in favour of our above proposal. In this picture, well-developed reactive areas ('pits') are observed, which are more clearly structured than has been found so far. In most cases, only one relatively large copper-rich grain is to be seen within each of these pits. According to our recent XRD results on $CuCl_2$ containing contact masses,[4] these particles must consist of η-Cu_3Si. It is a key observation that these particles within the reactive areas are surrounded by a region which is characterized by a very low copper concentration, hardly higher than outside the reactive pits, i.e. on the silicon surface which had not been attacked. In this copper-poor environment of the η-Cu_3Si particles, silicon has been consumed, resulting in the formation of the pits. It has to be concluded that the reaction must have taken place in that copper-poor region, and not at the η-Cu_3Si particles. As an alternative interpretation, one could argue tentatively that silicon had been diffused away from this region towards the η-Cu_3Si particle, in order to react there with methyl chloride. However, the driving force of such diffusion could only be the silicon concentration difference between the silicon surface and the η-Cu_3Si surface. It is quite unimaginable that only this concentration gradient would be able to detach silicon atoms from the very stable crystal lattice at only 340 °C and to transport them over long distances onto the η-Cu_3Si crystallites. On the other hand, it is easily conceivable that copper, which is essentially more mobile in the Cu/Si system and can easily diffuse on and into silicon surfaces,[21–23] diffused from the η-Cu_3Si particles onto the silicon surface, forming the active Cu–Si surface species there. This surface-alloying of silicon with copper seems to be the precondition of the synthesis reaction, acting either via the formation of Cu–Si pairs, necessary for a dissociative adsorption,[1] and/or via a weakening of the Si–Si bond.[7,23,24]

The above key observation was only possible by investigating a sample with such clear surface topography as the 20 min sample of $CuCl_2/Si_{tech}$/Zn. After 3 h (Fig. 4) the η-Cu_3Si particles had already dispersed, below the resolution of EDX, and reliable statements about copper concentrations on particles and between them were no longer possible with this method.

The increase of η-Cu_3Si dispersion, which took place between 20 min (Fig. 5) and 3 h reaction time (Fig. 4), is reminiscent of the analogous observation with contact masses containing copper oxalate as copper source.[4] The mechanism of this apparent η-Cu_3Si crystallite splitting is not yet clear. Possibly, the reaction itself is involved. It is conceivable that the reaction also proceeds on the η-Cu_3Si surface to a lower degree, connected with copper redistribution and redispersion processes. The possibility of the reaction on the surface of bulk η-Cu_3Si has been demonstrated.[25] However, considering our results and the fact that the reaction can also take place in the absence of η-Cu_3Si,[4,17] the proportion of the reaction taking place on η-Cu_3Si should be a minor one.

It is readily imaginable that such redispersion processes generally occur in η-Cu_3Si containing contact masses and that they finally lead to the Cu–Si surface species by spreading of copper species. In this sense, the three-dimensional, less active η-Cu_3Si crystallites could be regarded as a precursor of the two-dimensional, catalytically highly efficient Cu–Si surface species. Following this idea may make it possible to understand contradictions in the literature.

According to the above concept, the existence of free silicon surface, on which copper species can diffuse in order to form Cu–Si surface species, is a precondition of an effectively working contact mass. If the silicon surface is essentially covered by copper-rich species, a breakdown of the reaction results (see Fig. 3). High and stable rate of the reaction is observed in contact masses with distinct reactive areas, surrounded by a free (still not attacked) silicon surface.

It is interesting to compare this concept with the model of Voorhoeve[1] from the 1960s period. Voorhoeve proposed the existence of a free silicon surface as a precondition of high reaction rates, too. His model was based on the assumption of a catalytically active η-Cu_3Si surface and of a lateral diffusion of silicon towards η-Cu_3Si. This difference was thought to maintain a sufficiently high silicon concentration at the η-Cu_3Si surface. Also, in this model, the reaction breaks down when the silicon grains are essentially covered by copper-rich species like η-Cu_3Si, e.g. when the major part of the silicon has already been consumed by the reaction.

Either of the two models predicts a breakdown of the reaction, if the silicon grain surface is essentially covered by high amounts of copper-rich species. The models differ mainly in the assumption about the function of the free silicon surface. According to Voorhoeve, this free surface is needed to ensure lateral silicon diffusion. In our model, the free surface is necessary for the formation of Cu–Si surface species, e.g. by copper surface diffusion. This means that the two models differ only in the assumption about the relative mobility of the Si and Cu atoms. The far higher mobility of Cu atoms in the Cu/Si systems,[22,23] which was shown only after Voorhoeve's work, seems to be in favour of our proposal.

The promoter zinc as a moderator of the Rochow reaction

Over decades of scientific work on the Rochow synthesis, a number of proposals have been submitted concerning the mode of action of the promoters for this reaction. The action of promoters has been discussed in very different ways; the following short survey certainly is not complete. In the 1960s the action of trace amounts of the promoters aluminium, indium, gallium, phosphorus, antimony, bismuth and lead was interpreted in terms of the electronic theory of heterogeneous catalysis.[1] The promotors zinc, aluminium and antimony were assumed to take part in the surface chlorination of silicon.[26] According to Ref. 18, zinc and aluminium could catalyze the formation of the intermediate CuCl from copper and the alkyl chloride. A zinc species may act as a methylating agent,[27] or it may direct the dissociative adsorption of methyl chloride.[14] Tin was suggested to promote the reaction synergistically with zinc or aluminium, by reducing the surface tension and by increasing the dispersion of metal alloys.[27] In the presence of zinc, the silicon diffusion is no longer rate-limiting,[25,28] and carbidic carbon is converted into graphitic carbon, setting free active sites in this way.[8] According to Ref. 5, promoters decrease the segregation energy of silicon in copper silicides and cause a silicon enrichment on the surface. Finally, promoters could influence the crystal growth of copper silicides.[29] At present, it is difficult to decide which of these hypotheses describes the reality. Often they propose a real acceleration of the reaction rate by the promoter. In the following, we will examine this more general statement and submit an alternative proposal for the action of the zinc promoter.

As has been demonstrated in Fig. 1, the steady-state activity of $CuCl_2/Si_{tech}$ is distinctly lower than that of $CuCl_2/Si_{tech}/Zn$. However, at the same time the Figure demonstrates that this difference results exclusively from a difference in the time course of the activity of these two contact masses. The activity of the non-promoted sample increases steeply at the very beginning to high values, but it declines after a short period to a low steady state. Unlike $CuCl_2/Si_{tech}$, the zinc-promoted $CuCl_2/Si_{tech}/Zn$ reaches a high steady-state activity, stable for hours, without such complicated time dependence. These results reveal the real function of zinc. The promoter did not act as an accelerator of the reaction rate. In the initial period, perhaps the latter could have been even higher in the absence of the promoter; see Fig. 1. Apparently, the problem is not to accelerate the reaction, but to ensure the stability of the reaction rate at a sufficiently high level. Just this is the task of the rate promoter.

From Figs 3–5, the mode of action of the promoter can be understood. The surface of $CuCl_2/Si_{tech}$ is practically completely covered by species with high copper content. The detrimental action of such strong copper coverage is explained in the preceding section by our model of active Cu–Si surface species. As was demonstrated by its high initial activity, the surface of this sample was very reactive at the very beginning. Copper species were able to attack the whole of the surface and to cover it. There remained hardly any possibility of a lateral diffusion of copper species to form the active, highly dispersed or two-dimensional Cu–Si species. Because of a lack of free silicon surface, the reaction declined. Unlike the non-promoted $CuCl_2/Si_{tech}$ (Fig. 3), the surface of $CuCl_2/Si_{tech}/Zn$ (Fig. 4) looks similar to non-promoted $CuCl_2/Si_{pure}$ (Fig. 2), i.e. distinct reactive areas can be observed. Hence, copper species were able to diffuse towards non-attacked free silicon surface and to form Cu–Si surface species, which guarantee high and stable activity.

In greater detail, the action of the promoter could be as follows. $CuCl_2/Si_{pure}$ and $CuCl_2/Si_{tech}$ only differ by the presence of silicon impurities in the latter. Hence, the high initial activity of $CuCl_2/Si_{tech}$ as well as the following fall in activity should be due to the action of the silicon impurities. One could imagine that the impurities disturb the protecting native oxide layer on the silicon grains and make the whole of their surface very reactive. In this way, a high initial activity develops but, on the other hand, the whole of the surface will be covered by copper, until the reaction declines. Zinc, probably as zinc chloride, seems to be able to neutralize this catalytic, but ultimately detrimental, action of the impurities. It prevents the blanket attack on the surface and localizes the reaction to the known pits. The impurities are known to be oxides of several metals. It is interesting to remember that zinc chloride is used as a flux in soldering procedures, because of its ability to remove oxide layers from metal surfaces, according to the reaction $ZnCl_2 + MeO \rightarrow Me[ZnCl_2O]$.[30] After the impurities are neutralized by the promoter, the contact mass is similar to an Si_{pure}-containing one, i.e. the reaction is restricted to the reactive pits. Silicon surface remains free for the formation of Cu–Si surface species and the contact mass activity remains essentially constant for hours.

On the whole, it seems that the well-known promoter zinc acts in fact not as an accelerator of the specific reaction rate, as has been believed up to now, but as a kind of moderator of the Rochow reaction, especially in the very first stage (‘induction period’). The promoter neutralizes the action of silicon impurities, localizes the reaction to demarcated pits on the surface, keeps silicon surface free, and helps to maintain a sufficiently high and stable activity of a contact mass in this way. It is, of course, an open question whether this mode of action applies to other promoters as well, and whether the promoter zinc can also act in other ways. In a forthcoming paper, we will compare the promoter action of zinc with that of caesium.

CONCLUSIONS

Non-promoted and zinc-promoted Rochow contact masses based on pure and on technical-grade silicon were investigated by the spatial resolution techniques SEM–EDX and SAM–AES.

Places on the contact mass surface where the reaction took place could be identified and analyzed. These reactive regions proved to be very poor in copper. This finding gives direct evidence of the existence and the catalytic action of (X-ray)-amorphous Cu–Si surface species, i.e. extremely highly dispersed Cu–Si particles or two-dimensional species such as Cu–Si surface compounds, which we proposed recently. Ascribing the catalytic activity of Rochow contact masses to such species makes it possible to explain contradictions in the literature concerning the role of XRD-detectable Cu–Si phases such as η-Cu_3Si. The role of η-Cu_3Si as a catalytically active species seems to be a minor one, but it could act as a copper reservoir for the formation of the active Cu–Si surface species.

The mode of operation of the zinc promoter can be understood as a moderating action rather than as a real accelerating one. The promoter ensures a sufficient stationarity of the reaction. It seems that zinc neutralizes the detrimental action of silicon impurities. The silicon impurities make the whole of the silicon surface reactive and in this way cause a general blockade of the silicon surface by copper species after a short time. The promoter moderates the reaction by restricting it to demarcated reactive surface pits. The silicon surface remains partly free, and active Cu–Si surface species can be formed by lateral diffusion of copper species onto silicon surface that is still free.

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