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η-Cu_3Si Percentage and Particle Size in Various Rochow Contact Masses

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Various Rochow contact masses have been characterized by catalytic tests as well as by X-ray diffraction with respect to η-Cu_3Si percentage and particle size. The presence of η-Cu_3Si in the contact masses is neither a necessary nor a sufficient precondition of catalytic activity, but a certain contribution of dispersed η-Cu_3Si to the activity cannot be excluded. The results can be explained consistently by assuming highly dispersed or even two-dimensional Cu–Si species, not detectable by X-rays, as catalytically active species. The promoters zinc, antimony and tin do not significantly change the percentage and particle size of η-Cu_3Si.

Keywords: Rochow reaction; contact mass; copper silicides; η-Cu_3Si; X-ray diffraction; particle size

INTRODUCTION

The Rochow process has been industrially realized for decades and supplies the silicone industry with methylchlorosilanes (Eqn [1]; $x+y+z=4$),

$$Si_{powder}+CH_3Cl_{gas}\xrightarrow{\text{copper catalyst}}(CH_3)_xH_ySiCl_z \quad [1]$$

which are the precursors for the huge diversity of silicone products. The most desired product is dimethyldichlorosilane (DDS; $x=2$, $y=0$, $z=2$).

The process is based on the reaction of the 'contact mass' (c.m.), i.e. the mechanical mixture of silicon powder, a copper component (copper powder or compounds) and promoters (e.g. zinc, antimony, tin) with methyl chloride in fluidized bed reactors. In the so-called 'induction period', i.e. the very first reaction period, during which the catalytic activity develops, the copper component converts into a catalytically active species, fixed on the surface of the silicon grains. Despite numerous papers on the subject, reviewed for example in Refs. 1–3, and despite its great industrial importance, the Rochow reaction and the mode of action of the contact mass have been poorly understood. This might be due to the exceptional situation that a solid, i.e. silicon, participates as a reactant in a catalytic reaction. There are a number of basic problems, which are still under investigation, including the nature of the catalytically active component and surface as well as the reaction mechanism.

The Cu–Si phase, η-Cu_3Si, has frequently been found in contact masses and has been discussed as a catalytically active component for decades. The idea was originated by Trambouze[4] and coworkers, who observed correlations between the η-phase and the catalytic performances of contact masses and proposed a dissociative adsorption of methyl chloride ($CH_3\rightarrow Cu$; $Cl\rightarrow Si$) on the Cu_3Si surface as an important reaction step. Klebansky and Fikhtengolts[5] as well as Voorhoeve[1] and coworkers established a mechanism with the reverse polarization ($CH_3\rightarrow Si$; $Cl\rightarrow Cu$). The clarity of their model may have contributed to its acceptance. But, from the very beginning, there were also doubts. Müller and Gümbel[6] could not confirm the importance of η-Cu_3Si. A Russian school (e.g. Ref. 7) rejected this hypothesis, too, and ascribed a role in the copper redistribution processes within the contact mass to the η-phase. These authors assumed surface-chlorinated silicon species as active sites. Recent SEM[8] and SEM/XPS/Auger[9] investigations by Banholzer *et al.* did not decide the question as to whether η-Cu_3Si is the active species in real contact masses, or left doubts about the importance of this species, respectively.

Falconer's group indeed demonstrated that methylchlorosilanes can be produced on massive Cu_3Si from methyl chloride (e.g. Frank Ref. 10). However, in accordance with our preliminary note,[11] this finding does not necessarily mean that Cu_3Si is also the active component in real,

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powder-like contact masses, where various copper species of possible catalytic relevance can be formed from the original copper component during the induction period. Furthermore, Frank *et al.*[12] proposed that the Cu_3Si surface is not active itself, but only delivers an underlay for the formation of active sites, which were assumed to contain Si–Cl, Si–Cu and Si–C bonds. Finally, Floquet *et al.*[13] studied the Rochow reaction on Si(100) model surfaces in the presence of several copper catalysts. The authors discussed the role of η-Cu_3Si, but did not rule out the reaction without this phase as an intermediate.

With this paper, we would like to contribute to the knowledge on the η-phase problem. We determined the percentage and particle size of η-Cu_3Si in real, powder-like contact masses by X-ray diffraction after interrupting the reaction, and tried to correlate the results with the catalytic properties. We are aware, of course, that X-ray diffraction is not a surface-specific tool, the use of which would be highly desirable for the investigation of a heterogeneous catalyst. But, as long as knowledge on the active species in the Rochow system is in its present unsatisfactory state, information from a bulk method is valuable. There is a lack of results from chemisorption methods and modern surface methods. Because Rochow contact masses and their surfaces have very complicated compositions, morphologies and structures (e.g. Refs 8, 9, 11–14), such investigations are expensive and the results are still difficult to interpret (see also the Discussion section).

The catalytic properties of Rochow contact masses can dramatically and confusingly depend on quality and quantity of the c.m. components,[15] sometimes more than has been considered in the various papers. Therefore, we have included in this paper results from not only one, but from various, c.m. systems, in order to avoid the danger of drawing too general conclusions from too specific experiments. However, the results will be discussed exclusively with respect to possible relations between η-Cu_3Si and catalytic properties. It is not intended to give a complete survey of the properties of all the possible combinations of the c.m. components used, or to interpret the relations between composition and catalytic properties of the various c.m. types in detail. These relations are hardly to be explained up to now, and can be even more complicated, as can be seen from the results of this work. We would like to contribute to the solution of such open questions in forthcoming papers.

The reliability of any conclusions doubtless depends on the significance of differences in the properties of the specimens investigated. It was attempted to obtain these desired differences in the catalytic and/or in the structural properties of the contact masses by varying the reaction time, nature and percentage of the copper components, as well as the promoters.

EXPERIMENTAL

Copper components

Four copper components ('catalysts') were used for preparing contact masses: copper oxalate, 'CuOx', prepared according to Ref. 16 from *pro analysi* grade chemicals; a special copper powder ($0.9\,m^2\,g^{-1}$), 'Cu_{met}', produced from electrolytic-grade copper in vibrating ball mills (BFW Ohrdruf, Germany); and anhydrous copper(II) chloride, $CuCl_2$, and copper(II) oxide, CuO, both *pro analysi* (Merck, Germany). The original copper content in the contact masses was 5.0 wt%; exceptions are indicated.

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 highly pure, monocrystalline semiconductor silicon, 'Si_{pure}' (Wacker-Chemie, Germany), were used. The particle sizes of the two types of silicon ranged from 71 to 250 µm, with the size distributions within this range being practically equal.

Promoters

The following well-known promoters were applied, as pure metallic powders and with the usual standardized concentrations in the contact masses: Zn, 0.25 ± 1 wt%; Sb, 30 ± 3 ppm; and Sn, 30 ± 3 ppm. For dosing antimony and tin to the c.m., silicon powder 'diluted' metal powders were used, because of the low percentages. Errors in promoter dosage are, of course, included in the overall experimental error; see below.

Methyl chloride

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

Catalytic measurements

Catalytic measurements at normal pressure were carried out in a glass microreactor with a volume of 50 cm^3, constructed according to Ref. 17. 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 c.m. The arbitrarily chosen reaction temperature for comparing catalytic performances was 340 °C. The methyl chloride flow amounted to 2.7 l h^{-1}. The reaction products were analysed by on-line gas chromatography.

The errors in the reaction rates have mostly been less than ±15%. The reproducibility of the catalytic tests depends on the actual c.m. system. The accuracy of measurements with well-activated contact masses is essentially better (often less than ±5%) than with badly working ones. This might be due to the formation of more stable catalytically active species in the case of active samples. The results in this paper are average values of 2–5 measurements. All those differences in properties of contact masses, on which our conclusions are based, are significant in terms of error statistics.

Contact masses

The c.m. types $CuOx/Si_{tech}$, Cu_{met}/Si_{tech}, $CuCl_2/Si_{pure}$, CuO/Si_{pure} and CuO/Si_{tech} were prepared by mechanical mixing of the respective silicon powder, copper component and, if applied, promoter. The specimens were dried *in situ* and afterwards heated up to 340 °C in flowing methyl chloride. The gaseous reaction mixture was analysed every 15 min. The methyl chloride conversion was calculated according to Ref. 18. Total reaction rates r, as a measure of the catalytic activity of the contact masses, were calculated according to $r = Fx/W$ (F = mc flow rate; x = mc conversion; W = c.m. weight). The selectivity of the formation of dimethyldichlorosilane (DDS) was calculated as the molar ratio DDS/(DDS + methyltrichlorosilane + trimethylchlorosilane + methyldichlorosilane + dimethylchlorosilane).

X-ray diffraction

X-ray diffraction was performed in order to determine percentages and particle sizes of η-Cu_3Si as well as for the case of the copper powder based contact masses, of metallic copper. The X-ray data were obtained by means of an automated powder diffractometer HZG 4-A/URD 6 (Freiberger Präzisionsmechanik, Germany). No Cu–Si phases other than η-Cu_3Si could be detected in our contact masses.

For quantitative η-Cu_3Si analysis, the internal standard method has been applied, with TiO_2 (anatase) being the reference material. Using CuKα radiation, intensities were measured in the range $42° < 2\Theta < 57°$ for the two strongest η-Cu_3Si reflections and the three reflections of anatase occurring in this 2Θ range. For estimating particle sizes, the Scherrer formula was applied. By computer simulation of X-ray diagrams, we estimated that at 8 nm particle size just 3 wt% Cu_3Si and at 13 nm just 1.5 wt% Cu_3Si were detectable.

The corresponding catalytic experiments, (see above) were stopped at the desired reaction times by quickly cooling the microreactor to room temperature in flowing methyl chloride. A sample of the contact mass was mixed with a certain amount of anatase and immediately transferred into the sample holder of the diffractometer. The X-ray measurements were started a few minutes after opening the reactor. Because of its reaction with oxygen,[19] the X-ray reflections of η-Cu_3Si significantly weakened only after some hours. Nevertheless, this disappearance may have contributed considerably to the possible errors (*ca* ±25%) in the η-phase percentages.

RESULTS

Figure 1–4 give information about η-Cu_3Si contents and particle sizes in the various contact masses [parts (a)] and about total rates and DDS selectivities [parts (b)]. For the interpretation of the results, especially of those in Figs 3 and 4, it is necessary to know that the promoters by themselves (i.e. without a copper component) do not exhibit any catalytic activity under our experimental conditions.

In Fig. 1, results with $CuOx/Si_{tech}$ contact masses are depicted. With these experiments, the reaction time has been varied, from the very beginning up to the steady state of the reaction. It can be seen that η-Cu_3Si had already been formed

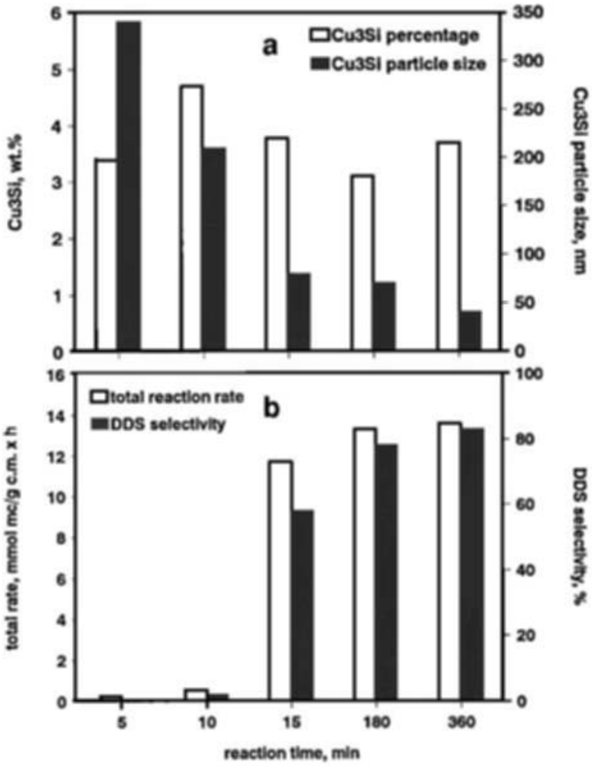

Figure 1 X-ray diffraction and catalytic investigation of CuOx/Si_{tech} contact masses with 5 wt% original copper content and 0.25 wt% zinc, after differing reaction times at 340 °C. (a) η-Cu_3Si percentage and particle size; (b) total reaction rate and DDS selectivity.

in the first minutes, but catalytic activity was not yet observed at that time. With elapsing time, the amount of η-Cu_3Si did not change decisively, but the particle size decreased strongly. At the same time, the catalytic activity and DDS selectivity developed and reached a steady state after about 1 h.

Figure 2 gives results with Cu_{met}/Si_{tech} samples. The amount of copper powder added was varied here. Activity and DDS selectivity of these samples are comparable with the other contact-mass types. However, with 3 and 6 wt% original copper content, no η-Cu_3Si could be detected, and with 12 wt%, only traces of Cu_3Si were found. It is striking that the total copper content, electrogravimetrically determined, and the metallic copper content, determined by X-ray diffraction, practically coincide. This means that copper species other than metallic copper could be present, only in rather low concentration. The particle size of that metallic copper amounted to >500 nm.

Figures 3 and 4 contain results with $CuCl_2/Si_{pure}$ and CuO/Si_{pure} contact masses, respectively. In Fig. 4, experiments with CuO/Si_{tech} are also included. Variations to catalytic properties and Cu_3Si properties were attempted by the addition of the promoters zinc, antimony and tin.

In Fig. 3(a), Cu_3Si percentages and particle sizes are given for non-promoted and promoted $CuCl_2/Si_{pure}$ contact masses. The percentages are relatively high; practically all of the copper added has been converted into Cu_3Si. Considering the possible statistical uncertainty of the X-ray measurements, the differences in the Cu_3Si properties are low at best; the corresponding catalytic results in Fig. 3(b) do not exhibit large differences either, except in the total rate with $CuCl_2/Si_{pure}$/Sb. Hence, the results in Fig. 3 do not demonstrate a credible influence of promoters on Cu_3Si properties and are by themselves hardly suitable for discussion of relations between Cu_3Si and catalytic properties. If compared with experiences with other non-promoted c.m. systems (see e.g. Fig. 4), reaction rate and DDS selectivity on the non-promoted system $CuCl_2/Si_{pure}$ are surprisingly high and the influence of the promoters on the reaction is surprisingly low. The latter findings will also be considered in a forthcoming paper on the mode of action of promoters.

Figure 4 gives the corresponding information for the CuO/Si_{pure} and CuO/Si_{tech} systems. The Cu_3Si percentages in these samples are distinctly lower (*ca* 50%) than in the $CuCl_2$-containing systems and do not significantly differ, either with different promoters or with variation in silicon quality. It cannot be concluded with certainty whether the silicon quality influences the Cu_3Si percentages, but seemingly the particle sizes are somewhat lower with the technical-grade silicon. Unlike Fig. 3(b), the corresponding catalytic results in Fig. 4(b) vary dramatically if promoters are added. Very low and very high activities and DDS selectivities occur. Zinc increases the originally very low reaction rate by a factor >6, accompanied by a jump in DDS selectivity. Also, antimony increases the catalytic performances several-fold. It is striking that, among all the results in Figs 3 and 4, the system CuO/Si_{pure}/Zn exhibits the highest reaction rate, but contains the lowest amount of Cu_3Si, even with relatively large particles.

Promoter actions of tin could not be observed in this work. The action of tin seems to be restricted to synergistic interactions with other promoters such as zinc; see e.g. Refs 20, 21.

DISCUSSION

η-Cu_3Si presence and catalysis

The CuOx/Si_{tech} contact masses (Fig. 1) definitely already contained η-phase in first minutes, i.e. before the Rochow reaction started, in amounts comparable with active samples. Hence, the mere presence of Cu_3Si freshly formed *in situ* in Rochow contact masses is by itself *not a sufficient precondition* of their catalytic activity. The conclusion is that Cu_3Si either is not catalytically active or that it needs special modifications of its morphology or, as already quoted,[12] of its surface.

On the other hand, the results on the Cu_{met}/Si_{tech} samples (Fig. 2) demonstrate that Cu_3Si is *not* even *a necessary precondition* of catalytic activity. No η-phase—or, in one case, only traces—has been detected, but the specimens exhibited similar catalytic properties to the Cu_3Si-containing ones. One could argue that the η-phase in these samples had decomposed by air contact at room temperature, accompanied by formation of metallic copper,[19] during the short time between interruption of the reaction and the X-ray experiment. But this possibility can be excluded. (i) We checked that the η-phase in the contact masses remains detectable at least for hours in air. The detectability of Cu_3Si in other c.m. types demonstrates this relative stablity. (ii) It is not possible that a noticeable part of the metallic copper detected had been formed by decomposition of the η-phase at room temperature,[19] because the metallic copper particle size (>500 nm) exceeded by far the η-

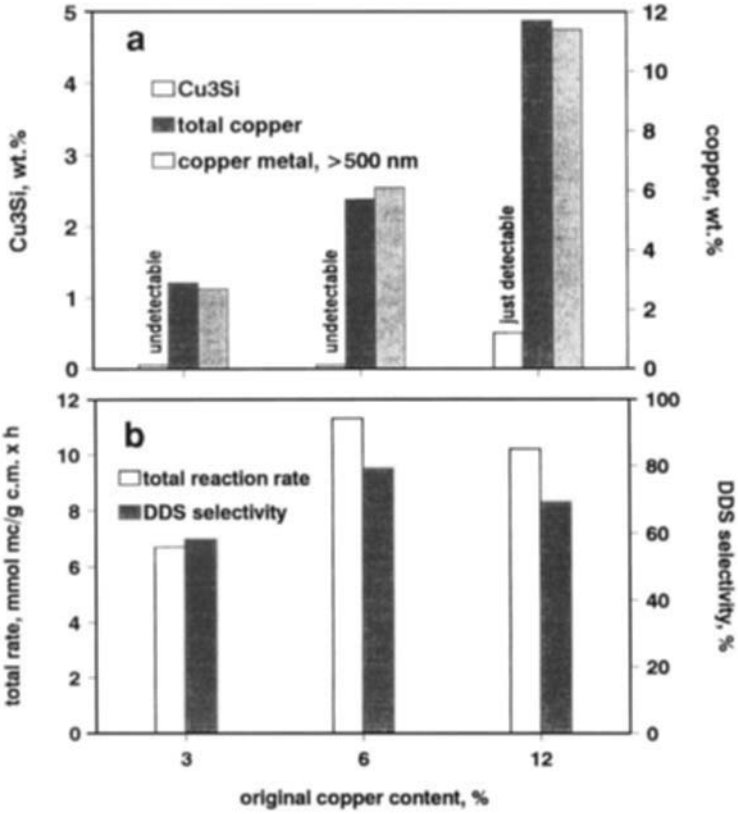

Figure 2 X-ray diffraction and catalytic investigation of Cu_{met}/Si_{tech} contact masses with differing original copper contents, promoted by 0.25 wt% zinc, after 3 h reaction time at 340 °C. (a) η-Cu_3Si and metallic copper (particle size >500 nm) content determined by X-ray diffraction, and total copper content determined by electrogravimetrical analysis; (b) total reaction rate and DDS selectivity.
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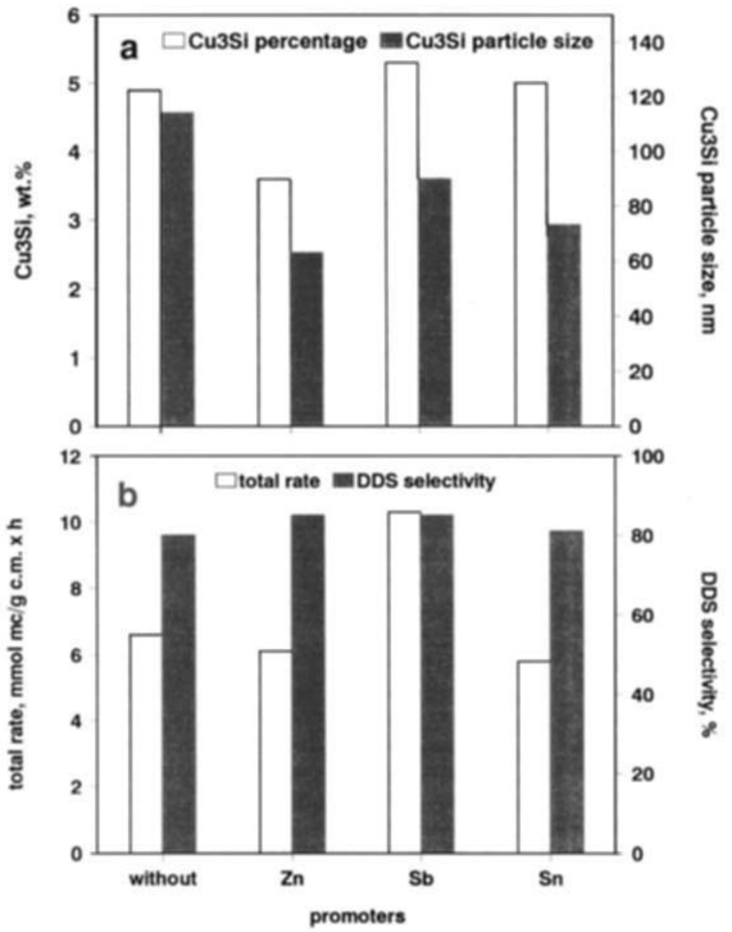

Figure 3 X-ray diffraction and catalytic investigation of $CuCl_2/Si_{pure}$ contact masses with 5 wt% original copper content, unpromoted and promoted by Zn, Sb and Sn, respectively, after 3 h reaction time at 340 °C. (a) η-Cu_3Si percentage and particle size; (b) total reaction rate and DDS selectivity.

phase particle size, which we usually found in active samples (*ca* 40–140 nm).

Furthermore, Fig. 2 demonstrates that the total copper content practically coincides with the metallic copper content. This means that copper species other than metallic copper including η-Cu_3Si particles with a size below the X-ray detectability, could have been present at most in rather small amounts in these samples. Because of its large particle size, >500 nm, the metallic copper can be ruled out as a catalytically active species. Hence, the catalytic activity of the copper powder based samples must be due to only rather small amounts of X-ray-undetectable copper species.

Possible role of dispersion of Cu–Si species

As shown, the catalytic activity of the Cu_{met}/Si_{tech} samples cannot be due to X-ray-detectable Cu_3Si, because this was not present. Only very low proportion of the copper added could have been catalytically active in these samples. If so, this small proportion of copper should have been highly dispersed, in order to exhibit a surface area large enough to bring about the activity observed. If one sticks to the reasonable concept of active copper silicidic species (e.g. Refs 1, 2, 4, 5, 10), one must assume that the active copper in the Cu_{met}/Si_{tech} contact masses exists as extremely small copper silicide particles or even as 'two-dimensional' Cu–Si surface compounds. Such species, referred to as 'Cu–Si surface species' in the following, would not be detectable by X-rays, because of their low content and their low dimensions. A long time ago, Gorbunov *et al.*[22] speculatively discussed Cu–Si surface compounds as active species.

The idea of low-sized or two-dimensional active Cu–Si species is plausible. The steady state of the Rochow reaction must be maintained by solid diffusion: Silicon is consumed by the reaction, and copper within Cu–Si species would necessarily enrich on the surface up to total blocking, unless solid diffusion prevented such enrichment. Falconer and coworkers[10] found that the solid diffusion limits the reaction rate on pure bulk-Cu_3Si. Of course, with low-sized Cu–Si species, the diffusion routes would be shorter and the diffusion resistances should be lower. This should favour the reaction.

The results of the investigation of the induction period on $CuOx/Si_{tech}$ contact masses (Fig. 1) could be taken as another indication of the role of dispersion of Cu–Si species. At just the same time as the catalytic activity developed, a significant

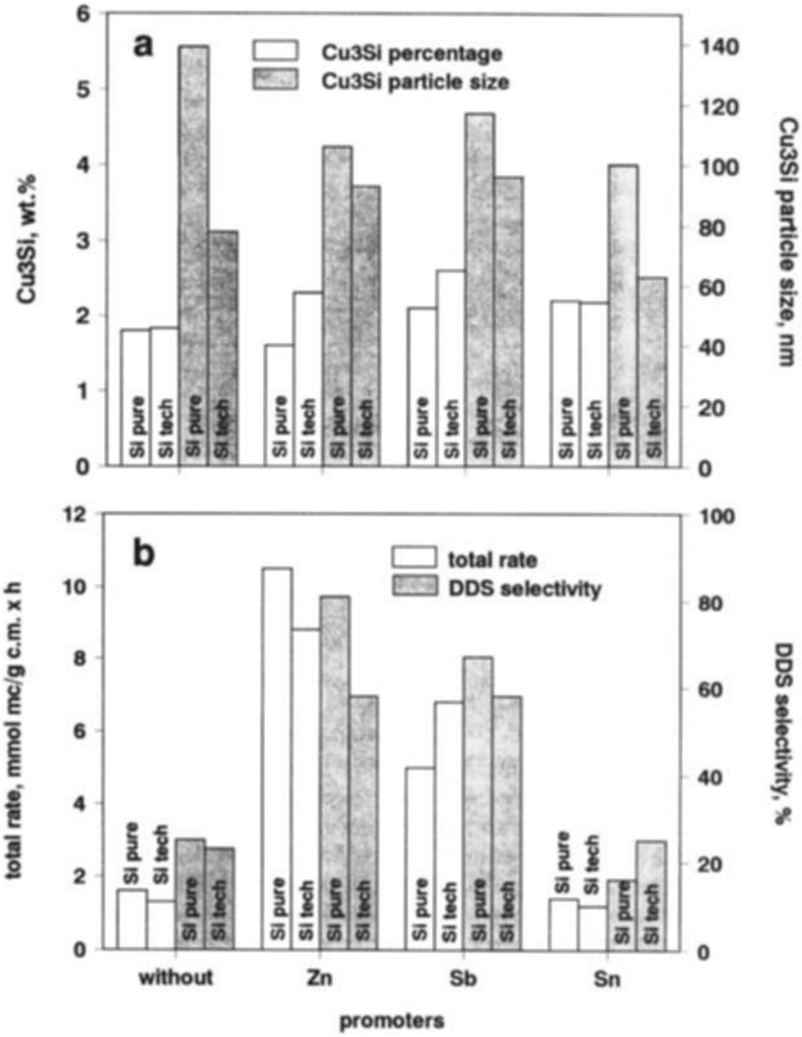

Figure 4 X-ray diffraction and catalytic investigation of CuO/Si_{pure} and CuO/Si_{tech} contact masses with 5 wt% original copper content, unpromoted and promoted by Zn, Sb and Sn, respectively, after 3 h reaction time at 340 °C. (a) η-Cu_3Si percentage and particle size; (b) total reaction rate and DDS selectivity.

decrease of the Cu_3Si particle size was observed. This would support the view that low-sized Cu–Si species are favourable for the reaction, for the reasons discussed above, and that the redispersion of coarse Cu_3Si may be an important element of the induction period.

However, accepting *dispersed* η-Cu_3Si as an active species, one is confronted with *two* possible carriers of the catalytic activity: dispersed X-ray-detectable Cu_3Si particles and extremely dispersed or two-dimensional Cu–Si surface species, the existence of which had to be concluded from the results with Cu_{met}/Si_{tech} samples.

Such a duality cannot logically be excluded. But, striving for a working hypothesis that is as simple as possible, one could also assume that the activity of Rochow contact masses is *in each case* mainly due to the Cu–Si surface species, not detectable by X-rays. This would mean that active contact masses *must* always contain Cu–Si surface species and *can* additionally contain X-ray-detectable Cu_3Si (or also other Cu–Si phases, e.g. Ref. 1), which is inactive or less active and which perhaps plays the role of a 'copper silicide pool', to be dispersed before becoming catalytically active. In this case, the redispersion which was observed during the induction period of $CuOx/Si_{tech}$ samples could be regarded as the beginning of a drastic redispersion process, which finally results in X-ray-undetectable active Cu–Si surface species.

According to the latter proposal, Rochow contact masses could contain the following Cu–Si species:

(a) coarse X-ray-detectable copper silicide (e.g. >300 nm), catalytically inactive;
(b) dispersed X-ray-detectable copper silicide (40–140 nm in this work), catalytically inactive or less active;
(c) Cu–Si surface species, i.e. extremely small copper silicidic particles, X-ray undetectable because of low content and size, and/or 'two-dimensional' Cu–Si surface compounds, catalytically active. These species participate in the total copper content of the contact masses only to a lesser degree.

η-Cu_3Si, promoters and impurities

The plausible idea that promoters and impurities, as well, could act by influencing formation or dispersion[23] of the possible key species η-Cu_3Si, was the background of the experiments with the standard promoters zinc, antimony and tin in $CuCl_2/Si_{pure}$, CuO/Si_{pure} and CuO/Si_{tech} contact masses (Figs 3 and 4). Apparently, the results do not support the above idea. The differences in η-phase percentage and particle size within each of the three above series are rather moderate and do not allow us to suggest a significant influence of promoters on Cu_3Si. Comparing the results of Si_{pure} with Si_{tech} samples, one could at best suspect that the silicon impurities can influence the properties of the η-phase, especially its particle size, to a certain degree. The differences observed in η-Cu_3Si properties, as far as they are significant at all, do not reasonably correlate with the catalytic tests, i.e. high (low) percentages or low (high) particle sizes cannot credibly be assigned to high (low) reaction rates or selectivities.

With the $CuCl_2/Si_{pure}$ contact masses, distinctly higher Cu_3Si percentages are observed than with the CuO/Si_{pure} and CuO/Si_{tech} samples. This means that the nature of the copper component influences the Cu_3Si percentage essentially more than promoters do. But, not even these distinct differences in the Cu_3Si percentages are reflected by the catalytic results. It is obvious that with the CuO-containing c.m. system, poor in Cu_3Si, very high reaction rates can occur, at least as high as or even higher than with the $CuCl_2/Si_{pure}$ system, rich in Cu_3Si. However, extremely low rates can also be observed in CuO-containing systems, in spite of only very moderate differences between the corresponding Cu_3Si properties. It is especially illustrative that $Cu/Si_{pure}/Zn$ exhibits the highest reaction rate among all the contact masses in Figs 3 and 4, but it contains the lowest amount of Cu_3Si, even with relatively large particle . Cu_3Si properties and catalytic properties do not correlate.

Assuming that the hypothesis of catalytically active η-phase was true, one should additionally check another hypothesis concerning a possible promoter influence on Cu_3Si. Following the ideas that, for example, chemical modifications of the Cu_3Si surface[12] or morphological modifications such as crystallite orientation[13] are necessary as a precondition of catalytic activity of Cu_3Si, one could assume that promoters can bring about such types of modifications. From this point of view, the six-fold increase in activity of CuO/Si_{pure} by addition of zinc, seen in Fig. 4(b), could be due to a modification of the η-phase or of its surface by suitable actions of zinc. However, this proposal is not supported by the experiments with the analogous $CuCl_2/Si_{pure}$ samples (Fig. 3). There, the catalytic properties of $CuCl_2/Si_{pure}$ without promoter and $CuCl_2/Si_{pure}/Zn$ are rather similar. In terms of the η-phase hypothesis, this different behaviour of the $CuCl_2/Si_{pure}$ system and the CuO/Si_{pure} system could only be explained by the speculative assumption that two Cu_3Si species, somehow differing from each other, had been formed in these two systems, the first of which is catalytically active by itself and can hardly be influenced by zinc, whereas the other one is poorly active, but can very effectively be activated by zinc addition. We do not have any indication of the real existence of such differing η-phase species. Also, the latter idea does not support either the hypothesis of a catalytically active η-phase or the assumption of an activating influence of promoter, in point of fact, zinc, on η-Cu_3Si.

Situation and prospects

We could suggest that η-Cu_3Si probably does not play that important role in the Rochow reaction which has often been ascribed to it. Although we cannot exclude a certain activity of *sufficiently dispersed* η-phase in some cases, the presence of Cu_3Si is apparently neither necessary nor sufficient and the action of promoters is seemingly not due to an influence on this species. This result is, of course, essentially a negative one. As an alternative, we have proposed the existence and catalytic action of low-dimensioned 'Cu–Si surface species'. This proposal is based on a logical deduction and not on direct evidence.

More direct evidence would require, for example, surface science methods and/or chemisorption methods, as is generally desirable in heterogeneous catalysis, but the application of such characterization methods is complicated in the case of the Rochow system. Even without mentioning that the contact masses are very sensitive to oxygen, some other peculiarities must be considered.

Copper, which must be a necessary component of the catalytically active sites, can exist in Rochow contact masses as various species. Different kinds of silicidic copper, metallic copper and perhaps also small amounts of copper (surface) compounds must be taken into consideration, and all of them can probably occur in varying portions and varying dispersion states. Moreover, it follows from this work, and has often been suspected in industrial practice, that only a rather low proportion of the c.m. total copper content is actually involved in the catalytic process. Hence, the methods to be applied must be able to distinguish between these various copper states and must be sensitive enough to identify and to quantify them, in order to find out the decisive species by correlating the results with catalytic data.

Furthermore, it is known (e.g. Refs 8, 9), that the Rochow reaction proceeds in the micrometer sized 'pits', etched into the silicon grain surface by the reaction and covering only parts of it. The catalytically active species must act exclusively within these small pits or only in parts of them. This means that a surface tool which provides only overall information over the whole of the surface may produce misleading results. Consequently, high spatial resolution methods are to be recommended for the Rochow system, all the more so as structure and topography of the surface strongly change with the c.m. composition and reaction conditions.

The above problems can be overcome by investigating real contact masses with suitable (*in situ*) surface and chemisorption/thermodesorption methods, preferably by combining them with each other and with catalytic experiments. Chemisorption has not yet been applied, but there have already been several interesting papers which made use of surface methods. XPS and Auger spectroscopy on model surfaces of massive Cu_3Si have yielded valuable information. The copper oxidation state on these surfaces has been found to be formally zero.[14,19] A bond polarity as $Cu_3^{\delta+}$–$Si^{\delta-}$ could be deduced.[14] Cu_3Si surfaces are enriched in silicon,[14,24] and promoters can influence this enrichment.[14] By alloying with copper, the Si–Si bond is weakened,[14,24] and the silicon reactivity is increased.[19] Surface atomic ratios of relevant elements after reaction with methyl chloride could be determined, resulting in proposals for the nature of active sites.[12] As mentioned, on Si(100) surfaces the action of several copper components on the Rochow reaction has been studied by XRD, SEM, EDS and AES.[13] The role of Cu_3Si as an active species has been discussed, but a parallel process without η-phase as an intermediate has not been ruled out. On the other hand, there have been only a few attempts to apply surface methods to powder-like contact masses. XPS measurements have demonstrated that the copper oxidation state is zero also in real contact masses.[25] By TEM and SEM as well as

XPS and Auger spectroscopy, the formation of active areas on the silicon surface have been investigated and atomic ratios of relevant elements within these areas[8,9] have been determined. The above papers gave a remarkable new insight into the Rochow system. However, the problem in this paper, i.e. whether η-Cu_3Si is actually catalytically active in real Rochow contact masses, could not yet be solved by surface methods, for the reasons mentioned above. We intend to give more direct evidence of our conclusions in future work.

CONCLUSIONS

In Rochow contact masses of different composition and history, large differences in η-Cu_3Si percentage and particle size can be observed by X-ray diffraction. However, the catalytic properties do not correlate with the X-ray results. On the other hand, contact masses with similar η-phase properties can exhibit strongly differing catalytic properties.

The mere presence of η-Cu_3Si freshly formed *in situ* in a contact mass is *not a sufficient precondition* of the catalytic activity, *neither* is the presence of η-Cu_3Si *a necessary precondition*. If potentially active at all, X-ray detectable copper silicide needs appropriate modifications in the induction period, in order to become active. Cu_3Si redispersion may possibly be such a modification.

An assumption of active, extremely dispersed or even two-dimensional Cu–Si surface species, not X-ray-detectable, had to be made and allows us to explain the experiments consistently. These species participate in the total copper content of the contact masses only to a low degree. If present, additional activity of dispersed η-Cu_3Si cannot be excluded.

The promoters investigated do not cause significant X-ray-observable changes of the η-phase percentage and particle size, but can cause dramatic changes of the catalytic properties.

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