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Interaction of Alkali Salt Promoters and Silicon Impurities in Rochow Contact Masses

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Cesium chloride- and rubidium chloride-promoted Rochow contact masses based on both technical-grade and highly pure silicon have been investigated in the Rochow reaction and by REM/EDX surface analysis. The alkali-salt promoters seem to act analogously to the well-known zinc promoter, by localizing the reaction to distinct reactive areas and keeping free the surface area for the reaction, probably for the formation of catalytically active Cu–Si surface species. The alkali salts exhibited their promoting action only in combination with the impurities within the technical-grade silicon. Otherwise, they acted as blocking poisons. The promoter action of alkali chlorides in contact masses based on technical-grade silicon is possibly connected with the formation of salt melts, containing alkali chlorides and impurities. These melts, analogously to zinc chloride, could dissolve oxidic impurities from the silicon surface which otherwise would enhance the blocking of potentially active surface by extensive copper deposition. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

The Rochow process

$$\mathrm{Si_{powder}} + \mathrm{CH_3Cl_{gas}} \xrightarrow{\text{copper catalyst}} (\mathrm{CH_3})_x\mathrm{H}_y\mathrm{SiCl}_z \quad x + y + z = 4$$

produces the raw materials for the whole of the silicone industry. It is based on the reaction of a mechanical mixture of silicon, a copper component and promoters, called the “contact mass”, with methyl chloride in fluid-bed reactors.

The reaction itself and the processes in the working contact mass have been poorly understood, despite numerous relevant papers (see e.g.[1–3]). One of the unsolved problems is the mode of operation of the promoters. There are numerous differing proposals in the literature to explain promoter actions.[1,3–10] At present, it is not yet possible to judge about the reality of these proposals in detail. It is not even possible to decide whether more than one, and if so how many, independent promoter mechanisms exist, and whether one promoter can act also in more than one way. A significant group of these hypotheses suggest a more or less direct interference of the promoters into the reaction mechanism, resulting in a real acceleration of the chemical reaction rate.

By our recent investigation,[11] on which we comment in this paper, we showed that the famous Rochow promoter zinc does *not* act as a real accelerator of the reaction rate. It turned out that zinc acts as a kind of structural promoter and rather as a moderator than as an accelerator. Zinc keeps a sufficiently large part of the silicon surface free of copper species, which act as poisons if their coverage and thickness become too high. Free silicon surface is necessary for the formation of Cu–Si surface species, which seem to be catalytically active and more important than X-ray-detectable Cu–Si phases such as η-$\mathrm{Cu_3Si}$.[11,12]

Moreover, we showed in this recent paper that the action of zinc has something to do with the

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presence or absence of impurities in the silicon. Contact masses based on highly pure silicon achieve a relatively high stable activity even in the absence of a promoter. Technical-grade silicon contact masses without promoter lose their initially high activity after a short time and then exhibit low reactivity, but zinc-promoted contact masses from technical-grade silicon reach high and stable activities. Hence, there seems to be a certain interaction between the promoter and the silicon impurities. The promoter neutralizes harmful action of the impurities.

In this paper, we would like to show that such interaction of promoters with impurities is not restricted to zinc as a promoter, but seems to be of more general importance. Moreover, we will demonstrate that there are cases where not only the promoter neutralizes detrimental impurity influences, but also a real co-operation between the promoter substance added and the silicon impurities seems to be necessary to bring about the real promoter effect. We will demonstrate this by means of the example of alkali-salts which were recently proposed as new Rochow promoters.[13] Hitherto, little has been done towards understanding the action of these new promoters, although an important role of the chemistry of the molten alkali-chloride promoters has been suggested.[14]

EXPERIMENTAL

Materials

The contact masses were prepared by mixing the silicon with the respective copper compound ('catalyst') and, if applied, the promoter. Two silicon charges were used: a highly pure polycrystalline silicon of semiconductor quality, $\mathrm{Si_{pure}}$ (Wacker-Chemie, Germany) and a technical-grade silicon, $\mathrm{Si_{tech}}$ (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). The particle sizes of the two samples ranged from 71 to 250 μm. Copper was added either as anhydrous copper(II) chloride, $\mathrm{CuCl_2}$, or as copper(II) oxide, CuO (Merck, Germany). The original copper content in the contact masses was 5.0 wt%. As promoters, cesium chloride, CsCl (Fluka, Germany; $>$ 99.0%), rubidium chloride, RbCl (Fluka, Germany; $>$ 99.0%), and metallic zinc powder (ECKA AS 011, Germany; $>$ 99.5%) have been applied, mostly with a concentration of 0.5 wt% in the contact mass. The methyl chloride used ($\mathrm{CH_3Cl}$, $>$ 99.6%) was dried by molecular sieve 4-A.

Four basic types of contact masses have been investigated: $\mathrm{CuCl_2/Si_{pure}}$, $\mathrm{CuCl_2/Si_{tech}}$, $\mathrm{CuO/Si_{pure}}$ and $\mathrm{CuO/Si_{tech}}$, each of them prepared without or with one of the promoters mentioned above.

Catalytic experiments

Reaction rates for comparing catalytic performances were measured by means of a fluidized-bed reactor, described elsewhere.[15] A 10 g portion of the contact mass was loaded into the reactor, heated by a radiation furnace. The mixture was dried in a nitrogen stream at 150 °C for 30 min before methyl chloride was fed in. The flow rate of $\mathrm{CH_3Cl}$ was $2.7\ \mathrm{l\ h^{-1}}$. The reaction was carried out at 340 °C. The methyl chloride conversion and the product distribution of methylchlorosilanes were determined every 15 min by on-line gas chromatography.

The methyl chloride conversion was calculated according to Ref. 7. Total reaction rates r, as a measure of the catalytic activity of the contact masses, were calculated according to $r = Fx/W$ ($F = \mathrm{CH_3Cl}$ flow rate; $x = \mathrm{CH_3Cl}$ conversion into silane products; $W =$ contact mass weight), with x being less than 0.15 in all cases. In addition to the formation of silane products, on all contact masses methyl chloride cracking, indicated by the formation of methane and hydrogen chloride, took place at a rate of 0.2–0.4 mmol $\mathrm{CH_3Cl}$ per g contact mass per h. This rather low side reaction will not be discussed in this paper. The selectivity of the formation of dimethyldichlorosilane (DDS) was calculated as the molar ratio DDS/(DDS + methyltrichlorosilane + trimethylchlorosilane + methyldichlorosilane + dimethylchlorosilane). The errors in the reaction rates have mostly been less than ± 15%.

Determination of the surface composition

The combined use of scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy gave access to the surface composition of the contact mass after the reaction. The SEM studies were performed in a Cambridge Instruments S360 electron microscope, operating at a beam energy of 15 kV. The EDX experiments were carried out using a Delta Class Analyzer 8000 (KEVEX). The resolving power of EDX spot analysis has been

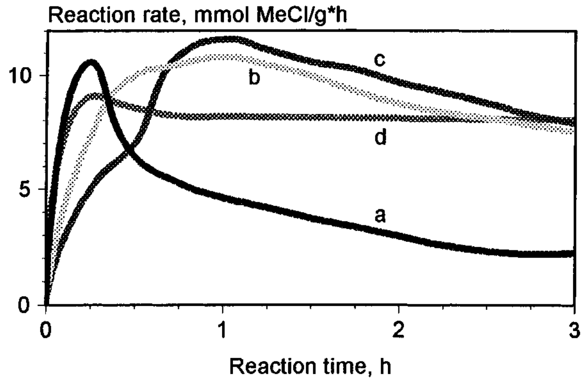

Figure 1 CH_3Cl consumption rates at 340 °C versus reaction time on the contact masses: (a) $CuCl_2/Si_{tech}$; (b) $CuCl_2/Si_{tech}/CsCl$; (c) $CuCl_2/Si_{tech}/RbCl$; and (d) $CuCl_2/Si_{tech}/Zn$.

about 2 µm. The EDX results are given as weight per cent within the spot analysed. Small amounts of the reacted contact-mass samples were analyzed in the microscope immediately after the catalytic experiments. The low amounts of oxygen taken up after short air contact do not significantly affect the surface composition with respect to copper and silicon.

RESULTS

Activity/time dependences of contact masses

In Fig. 1 the time courses of the catalytic activities of $CuCl_2/Si_{tech}$, $CuCl_2/Si_{tech}/CsCl$, $CuCl_2/Si_{tech}/RbCl$ and $CuCl_2/Si_{tech}/Zn$ are depicted (analogously to Fig. 1 in Ref. 11). The non-promoted system is characterized by a fast activity increase up to high values, but also by a dramatic loss of activity after the maximum. Unlike the latter, the alkali-promoted samples exhibit a stable activity at almost the level of the maximum of $CuCl_2/Si_{tech}$ over a long period, without this strong decline. That means that their behaviour is similar to the zinc-promoted $CuCl_2/Si_{tech}/Zn$ sample. It is clear that the low steady-state reaction rate with $CuCl_2/Si_{tech}$ is not a result of a generally low reactivity, but exclusively of the sharp decline after the high starting activity.

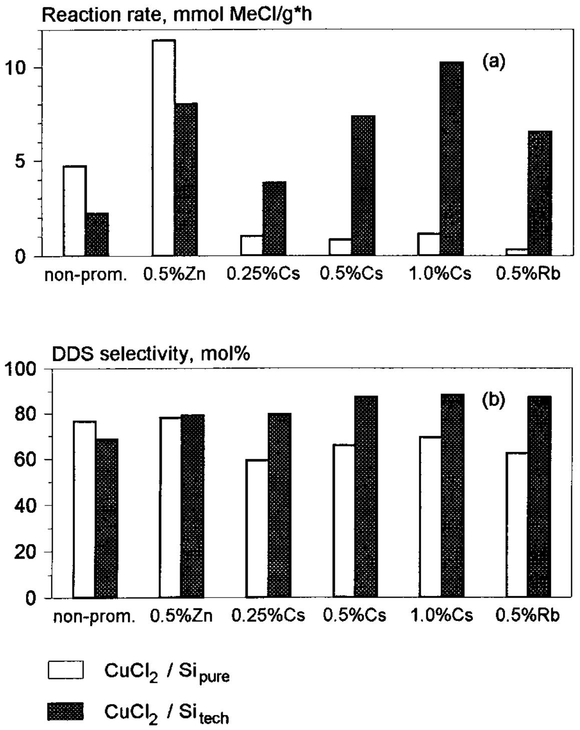

Figure 2 Reaction rates (a) and DDS selectivities (b) after 3 h of reaction at 340 °C on contact masses based on $CuCl_2/Si_{pure}$ and $CuCl_2/Si_{tech}$ with various promoters.

Steady state activities

For comparison, Figs 2 and 3 include catalytic activities (a) and DDS selectivities (b) after 3 h of reaction at 340 °C of non-promoted and promoted contact masses based on Si_{pure} and Si_{tech}.

Figure 2 gives the results for contact masses with copper chloride as the copper component originally added. Non-promoted $CuCl_2/Si_{pure}$ exhibits a stable medium activity. The corresponding non-promoted $CuCl_2/Si_{tech}$ is far less active than $CuCl_2/Si_{pure}$ after 3 h, due to its fast deactivation after the short period of high activity mentioned above. Zinc promotion causes high and stable reaction rates both with Si_{pure} and Si_{tech}. Unlike the zinc-promoted samples, with alkali-salt promotion dramatic differences are observed between contact masses based on Si_{tech} and Si_{pure}. With Si_{pure} addition of CsCl and RbCl leads to a strong poisoning of the activity, but in the case of Si_{tech} the alkali salts prove to be very efficient promoters, with the promoter action being proportional to its content, as can be seen with CsCl. The reaction rates on Si_{pure} and Si_{tech} differ by factors of up to about 20. One must be aware that

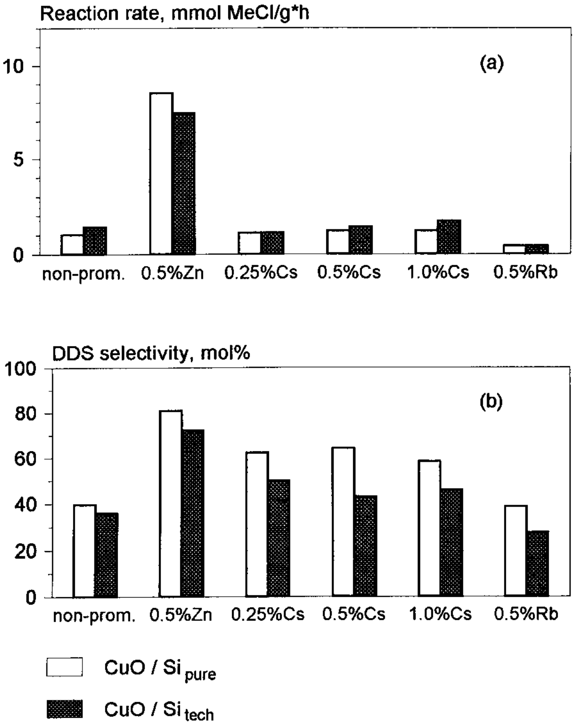

Figure 3 Reaction rates (a) and DDS selectivities (b) after 3 h of reaction at 340 °C on contact masses based on CuO/Si_{pure} and CuO/Si_{tech} with various promoters.

this huge difference can only be a more or less direct consequence of the presence of impurities in the technical-grade silicon, Si_{tech}.

The differences in the DDS selectivities are essentially more moderate than those in the reaction rates. These differences cannot be explained at present.

Figure 3 gives analogous results with CuO as the original copper component. Unlike the contact masses with $CuCl_2$, both the two non-promoted systems exhibit low reaction rates from the very beginning, the reasons for which are not presently understood.[12] Zinc increases the activity up to a level comparable with the $CuCl_2$ contact masses. In contrast to the efficient promoter action of alkali salts in $CuCl_2/Si_{tech}$ samples, the alkali salts are not able to activate the inefficient contact masses based on CuO.

SEM/EDX images

In Fig. 4 and Figs 5 and 6, respectively, SEM images of $CuCl_2/Si_{tech}$ and $CuCl_2/Si_{tech}/CsCl$ are to be seen.

The surface of non-promoted $CuCl_2/Si_{tech}$ (Fig. 4) is covered predominantly by copper species after running the Rochow reaction, just as we found recently.[11] The copper surface concentration on this

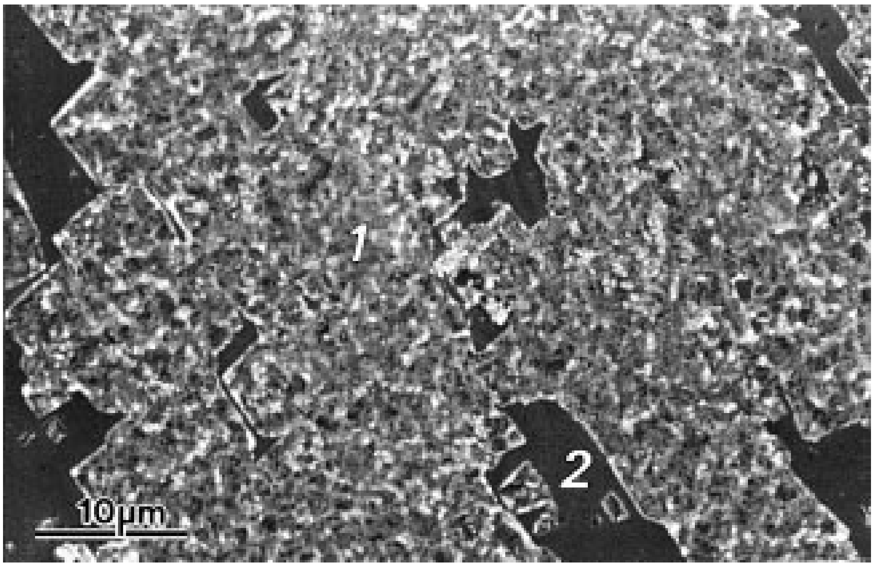

Figure 4 Scanning electron micrograph of non-promoted $CuCl_2/Si_{tech}$ after 3 h of reaction at 340 °C. EDX results of the reacted surface, covered by copper species (point *1*): 77 wt% Cu and 20 wt% Si; and of the non-reacted silicon surface (point *2*): 0.5 wt% Cu and 98 wt% Si.

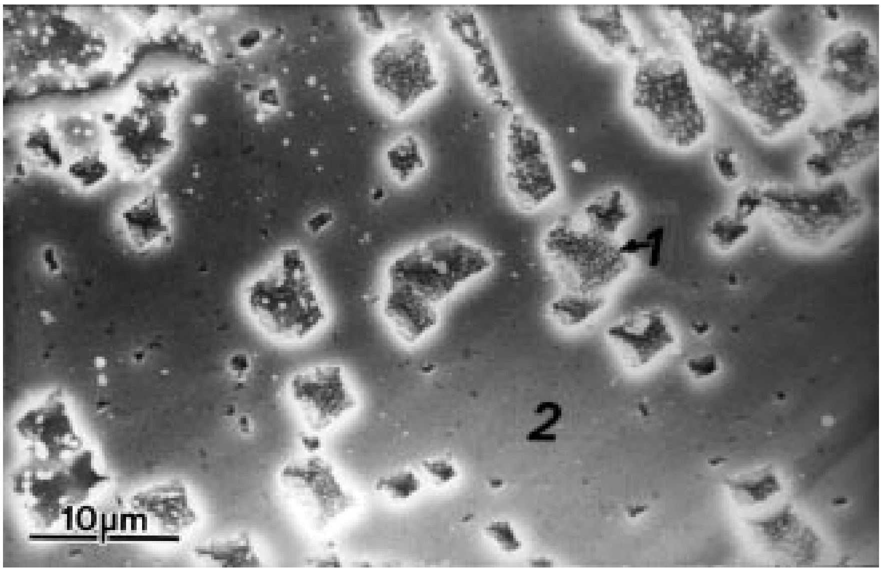

Figure 5 Scanning electron micrograph of $CuCl_2/Si_{tech}/CsCl$ after 3 h of reaction at 340 °C. EDX results of a reactive area with bright particles (point *1*): 12 wt% Cu, 1 wt% Cs and 75 wt% Si; and of the non-reacted silicon surface (point *2*): < 0.5 wt% Cu and 96 wt% Si.

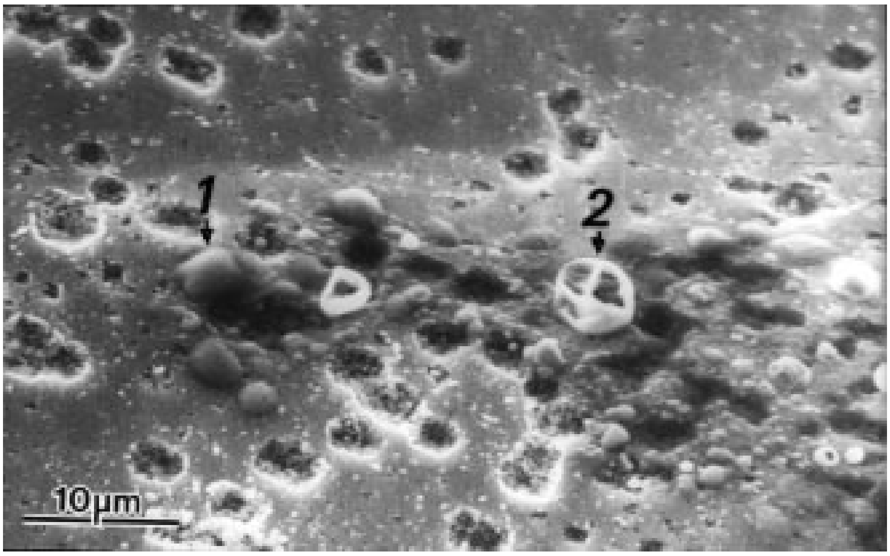

Figure 6 Scanning electron micrograph of $CuCl_2/Si_{tech}/CsCl$ after 3 h of reaction at 340 °C. EDX results for a dark blister (point *1*): 8 wt% Cu, 16 wt% Cs and 66 wt% Si; and of a hollow ball (point *2*): 19 wt% Cu, 37 wt% Cs and 35 wt% Si.

covered surface, measured by EDX, has been found to be at a high level between 70 and 84 wt% ($\approx$ 58 atom%) (see for example point *1* on the micrograph). Only a minor part of the silicon surface exhibited low EDX copper percentages (see point *2*), i.e. it did not react and remained free of blocking copper deposits.

In contrast to the non-promoted $CuCl_2/Si_{tech}$, the surface image of the cesium-promoted $CuCl_2/Si_{tech}/CsCl$ in Fig. 5 is typical for a normally working

Rochow contact mass. Distinct localized reactive areas, where silicon has been consumed by the reaction of silane formation, are surrounded by large copper-free areas, which have not reacted. This picture corresponds fully to the results with $CuCl_2/Si_{tech}/Zn$, described previously.[11] Figure 6 gives another view of the $CuCl_2/Si_{tech}/CsCl$ contact masses. This micrograph reveals surface structures like blisters and hollow balls, which doubtless result from species molten previously. These bodies are distinguished by high cesium and copper contents. The surface concentrations of copper and cesium in the blister were found to be 8 wt% and 16 wt% respectively, and of the hollow ball 19 wt% and 37 wt%.

DISCUSSION

Analogy between zinc and alkali - salt promoter

The results with the $CuCl_2$-containing contact masses showed that the non-promoted Si_{tech} system exhibited low steady-state activity, less than the corresponding Si_{pure} system. However, this low activity was not a consequence of a generally low reactivity of Si_{tech}. On the contrary, it proved to be very active even after a short induction period, but it rapidly lost its high activity afterwards. Unlike this non-promoted system, the corresponding alkali-promoted contact mass kept its high activity over hours. On the whole, it seems that the promoter did not really accelerate the reaction rate, but only ensured the stationary state of the activity. This behaviour is fully analogous to that of zinc-promoted $CuCl_2/Si_{tech}/Zn$.[11]

The SEM images help to understand these findings. $CuCl_2/Si_{tech}$ lost its initially high activity within a short time, because its surface was severely blocked by copper species. The surface of the contact mass was essentially blocked by these high amounts of copper. Unlike the non-promoted sample, a considerable surface portion of the cesium-promoted $CuCl_2/Si_{tech}/CsCl$ remained free. The reaction proceeded, localized to distinct reactive areas ('pits'). This observation is also in complete analogy to the zinc promoter.

These facts can be interpreted in terms of a model which assumes a certain catalytic action of the impurities on the silicon surface and a cleaning action of the promoter substances. The silicon impurities are able to catalyse the attack of copper species on the silicon surface, e.g. by disturbing its surface structure or by disturbing the protecting SiO_2 overlayer. If the impurities are present over the whole surface in a sufficient concentration, the whole surface will be attacked by copper species and will be blocked. The promoters, zinc or alkali salts, are able somehow to clean the silicon surface from the harmful impurities. The cleaned surface will be attacked by copper species only at a few points, resulting in the typical pit structure of a working contact mass surface. An essential part of the silicon surface remains free. This free silicon surface is necessary for the existence or the formation of the active Cu–Si surface species which are mainly responsible for the catalytic activity of Rochow contact masses.[12]

Co-operation of promoters and silicon impurities

The most remarkable experimental result is the impressive influence of the quality of the silicon on the effectiveness of promoter additions to $CuCl_2$-containing contact masses. The direction of the promoter action can even reverse, depending on the silicon quality. With pure silicon, CsCl and RbCl act as strong poisons. But with technical-grade silicon the alkali salts strongly enhance the reaction rate, with the effect of the promoter proportional to its concentration. This leads to extreme differences in the activity of Si_{pure}- and Si_{tech}-containing contact masses, with the reaction rates differing by factors of up to more than 20. Unlike the alkali salts, with the zinc promoter no pronounced differences can be observed between the two silicon qualities. Zinc increases the catalytic activity with both types of silicon, but at the same time it levels the activity differences which existed between the two non-promoted systems.

Thus, alkali salts can be poisons with pure silicon, but they can be strong promoters with technical-grade silicon. Taking into account that the two silicon types ultimately differ only in the absence or presence of impurities, one has to conclude that these impurities play a crucial role if alkali promoters are used. It seems that there is a real co-operation between the promoter substances added and the impurities. The alkali promoter alone does not work. Only with the combination [alkali salt + impurities] is there an effective promoter system.

CsCl and RbCl poison the catalytic activity of $CuCl_2/Si_{pure}$ far less than the DDS selectivity. Therefore, it seems to be reasonable to assume that their poisoning action consists in a mere blocking of catalytically active surface. If so, it seems to be reasonable to suggest that the promoter combination [alkali salt + impurities] acts by increasing active surface areas or keeping them free. This would be in agreement with our model of action of alkali promoters and of zinc promoter, proposed in the preceding section.

Limited analogy between zinc and alkali-salt promoters

First, the results with CuO as the original copper component once more confirm the strong dependence of contact-mass properties on the nature of the copper component.[16] This strong dependence also applies to the response of the system to the addition of promoters. Both of the non-promoted CuO-containing systems, based on Si_{pure} and on Si_{tech}, are of low activity. This is surprising in the case of Si_{pure}, which is remarkably active even in the non-promoted state if $CuCl_2$ is used as the copper component. The reason for the activity difference between the two copper compounds is not yet clear. As we could show,[12] η-Cu_3Si is formed in both the types of contact masses in similar amounts and similar states of dispersion. Hence, differences in the η-Cu_3Si state cannot be responsible for the activity difference. That means that the catalytic action of this phase is questionable. One could imagine that the oxygen from added copper oxide forms oxidic overlayers, impeding the reaction by blocking potentially active surface areas. Zinc as a promoter could overcome this blockade and thereby augment the reaction rate. Unlike zinc, the alkali salts are not able to act accordingly, neither with Si_{pure} nor with Si_{tech}. Hence, the analogy of the action of zinc and alkali-salt promoters is a limited one and there are also differences in their mode of action. This is discussed below.

Possible nature of promoter action and promoter–impurity interaction

The more detailed nature of the promoter actions and of the interaction between the alkali salts and the silicon impurities observed can only be discussed in a speculative way. As mentioned, the results allow us to propose some surface cleaning action of the promoters. The impurities, which are predominantly concentrated on the surface of the silicon crystallites, possibly act as nuclei for the attack of copper species on the silicon surface, which is normally protected by the native SiO_2 overlayer. If the impurity surface concentration is high, the surface will be attacked in many places and will be covered by copper species as a consequence. In cases of lower impurity concentrations, only a few places will be attacked. In such places, the known demarcated pits are formed, which grow in the course of the synthesis reaction. There remains sufficient space on the silicon surface for continuous formation of the active Cu–Si surface species, which according to our view are catalytically active.[12]

The cleaning action of the promoters could consist in a complexation of the silicon impurities. Zinc, which surely exists as zinc chloride in the working contact mass, could perhaps react according to $ZnCl_2 + MeO \rightarrow Me[ZnCl_2O]$,[17] where MeO denotes an oxidic impurity on the silicon surface. It is known that zinc chloride acts in soldering procedures in this way, too, i.e. it dissolves oxidic overlayers from metal surfaces. Such a reaction should preferably proceed in the liquid phase. It is remarkable that the melting point of zinc chloride (318 °C) is in the range of the reaction temperatures of the Rochow reaction. A role for molten-salt species has already been suggested.[14]

Actually, cesium chloride alone can hardly be imagined as a substance predestined to promote the contact mass surface in analogy to zinc chloride, or to poison it. Apart from its different chemical nature, this would be prevented anyway by its high melting point of about 638 °C and by its low vapour pressure. However, it is known that cesium chloride is able to form low-melting binary systems together with (for example) CuCl, which should be present in Rochow contact masses, at least during the induction period.[1] As an example, at the composition $CsCu_2Cl_3$ the system CuCl–CsCl melts at 274 °C.[18]

On the one hand, such molten species could block active surface areas and bring about in this way the dramatic loss of activity which is observed with CsCl addition to a non-promoted $CuCl_2/Si_{pure}$ contact mass (see Fig. 2). On the other hand, together with the silicon impurities these melts could act as promoters, somehow similar to zinc chloride. As to be seen from Fig. 6, it is evident that molten species were formed in a $CuCl_2/Si_{tech}$ contact mass which had been promoted with 0.5 wt% CsCl, resulting in high activity. Anyway, the alkali salts exhibit their promoting action only in the presence of impurities. However, at the same time the results show that the assumed promoter combination [alkali salt + impurities] cannot substitute for zinc chloride in each case. This promoter system seems to be unable, for example, to remove excessive oxide layers, which are possibly formed if copper oxide is used as the copper component.

It should be repeated that the above interpretation is a speculative one. Further research has to be done in order to check these assumptions and to understand promoter actions in Rochow contact masses more generally. Our model of 'cleaning salt' species would give an explanation of the mode of operation of such promoters, which are usually added to a contact mass in percentages comparable with the percentage of silicon impurities, i.e. zinc, aluminium, cadmium and alkali salts, say at 0.1–1.0 wt%. Other types of promoters, such as antimony or tin, which are added with percentages in the ppm range, probably act in other ways.

CONCLUSIONS

The mode of operation of cesium chloride and rubidium chloride as promoters of the Rochow reaction has been investigated. If effective, the alkali-salt promoters seem to act analogously to the well-known zinc promoter by localizing the reaction to distinct reactive areas and keeping free a sufficient portion of contact mass surface area for the surface reaction, probably for the formation of catalytically active Cu–Si surface species.

The alkali salts exhibited their promoting action only in combination with the impurities within the technical-grade silicon. Otherwise, they acted as blocking poisons.

The promoter action of alkali chlorides in contact masses based on technical-grade silicon is possibly connected with the formation of salt melts, containing alkali chlorides and impurities. These melts could dissolve oxidic impurities which otherwise would enhance the blocking of potentially active surface by extensive copper deposition, and could clean the silicon surface in this way.

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