

APCAT B3

Performance of silica-supported copper oxide sorbents for SO_x/NO_x-removal from flue gas

I. Sulphur dioxide absorption and regeneration kinetics

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Abstract

Sulphur dioxide absorption and regeneration kinetics of several silica-supported copper oxide (CuO) sorbents were studied in a microbalance over a temperature range of 300 to 450°C. The porous silica support was prepared according to a sol-gel technique, and CuO was deposited on this support through an ion-exchange technique to achieve a uniform, highly dispersed CuO deposition. During up to 75 cycles of oxidation, sulphation, and reduction, the ion-exchanged sorbents did not show a significant loss in chemical activity except for some deactivation in the first 1-3 cycles. The sulphation kinetics of the pre-oxidised ion-exchanged sorbents were found to be in agreement with literature data for impregnated alumina-supported CuO sorbents. In case of direct contact of reduced ion-exchanged sorbents with simulated flue gas, the simultaneous and fast oxidation was determined to have a large positive effect on the sulphation rate up to approximately 60% conversion to copper sulphate. This was mainly attributed to structural effects inside the CuO deposits. For the sulphated ion-exchanged sorbents, the reduction by hydrogen was identified as an autocatalytic reaction. The autocatalytic effect was also observed during the (much slower) reduction by methane, but there it was preceded by a period in which a second autocatalytic effect appeared. The reaction kinetics of the ion-exchanged sorbents developed were furthermore compared with experimental results of other silica-supported CuO sorbents prepared by vacuum impregnation and homogeneous deposition-precipitation.

Keywords copper oxide, flue gas desulphurisation, ion-exchange, kinetics, silica-supported copper oxide sorbent, thermogravimetric analysis

INTRODUCTION

Dry regenerative processes with a copper oxide (CuO) sorbent are among the advanced processes being considered as alternatives to the widely-used flue gas desulphurisation processes based on wet once-through limestone scrub-

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bing The CuO is deposited on a porous support to create an active sorbent with a high stability In the absorber of these processes, sulphur dioxide (SO_2) reacts with the supported CuO and oxygen to copper sulphate (CuSO_4) at 300–450°C Regeneration is carried out with a reducing gas, e.g. hydrogen, carbon monoxide or methane, the copper sulphate being reduced to metallic copper The rate of this reaction is sufficiently high at the same temperature as applied for the absorption, additional heating and/or cooling of the sorbent is therefore not required The regenerator off-gas is rich in SO_2 and can be further processed to produce sulphuric acid or elemental sulphur After regeneration, the sorbent can be oxidised and used for SO_2 absorption again

When compared to limestone scrubbing, CuO processes offer the advantages of (i) a small sorbent make-up, (ii) producing only a relatively small amount of salable by-product, and (iii) avoiding stack gas reheat and a large water consumption Furthermore, NO_x can be removed simultaneously by adding ammonia to the flue gas CuO and CuSO_4 act as catalysts for the selective catalytic reduction of NO_x [1,2]

To date several CuO processes have been and are being developed The main differences between these processes are related to the absorber design Already in the late 1960s Shell introduced the Shell Flue Gas Treating (SFGT) process with the characteristic parallel passage reactor; a cyclic operated fixed-bed contactor in which the sorbent is contained in parallel cages [3]. A CuO process with a fluidised bed absorber has been developed at the Pittsburgh Energy Technology Center (PETC) to enable continuous operation instead of the swing operation of the SFGT process [2,4,5] However, the pressure drop for the flue gas is higher when compared to the parallel passage reactor and the allowable superficial flue gas velocity is considerably lower [6,7]

We are studying the application of a relatively new contactor, the gas–solid trickle flow reactor [8]. In this reactor a dilute flow of solid particles is contacted counter-currently with the gas phase over a regularly stacked packing Favourable properties of the gas–solid trickle flow reactor are: (i) a low pressure drop, (ii) limited axial dispersion in the gas and solids phase, (iii) excellent heat and mass transfer between both phases, and (iv) counter-current operation Therefore, a gas–solid trickle flow reactor is expected to be an efficient absorber in a CuO process for the simultaneous removal of SO_x and NO_x from flue gases, in which the advantage of the continuous operation of the fluidised-bed process is combined with the low pressure drop and the high flue gas velocity of the SFGT process

The application of a gas–solid trickle flow reactor requires a special design of the sorbent First, the attrition resistance of the sorbent must be high and the sorbent particles must have an appropriate shape, preferably spherical, to enable a smooth particle flow through the reactor Secondly, the terminal velocity of the sorbent particles must be higher than the desired maximum flue gas velocity in the reactor This sets a minimum to the particle diameter at a

given particle density. Thirdly, the sulphation activity must be high for a maximum utilisation of the excellent gas-solids mass transfer in the absorber. Therefore a high intrinsic reaction rate is required as well as an open pore structure to limit the influence of pore diffusion on the overall reaction rate. Finally, the sorbent must be chemically and physically stable to withstand many sulphation-regeneration cycles. To satisfy these demands, several sorbents have been developed in a research project at the University of Utrecht [9]. They consist of a silica support, prepared by Shell according to a sol-gel technique [10], and copper oxide, deposited on the support through an ion-exchange technique [11,12].

The SO_2 absorption and regeneration kinetics of these "ion-exchanged" sorbents were studied in a microbalance set-up. To determine the influence of the applied CuO deposition technique on the sulphation activity of the sorbent, additional tests were conducted with silica-supported sorbents prepared by vacuum impregnation and homogeneous deposition-precipitation. Vacuum impregnation causes relatively large CuO deposits (20–50 nm diameter), which is generally expected to give a low sulphation activity. On the other hand, very small deposits (2–5 nm diameter) and probably a high sulphation activity can be created using the homogeneous deposition-precipitation technique [13], provided that very small support particles are applied with a large internal surface area. The support of the sorbents prepared by these two other techniques has not been optimised for application in the new flue gas treating process.

In this paper, the results of the microbalance experiments are discussed and compared with literature data. Special attention is paid to possible side-reactions, to the mechanisms of the reduction of CuSO_4 with hydrogen and methane, and to the effect of simultaneous oxidation and sulphation on the SO_2 absorption rate.

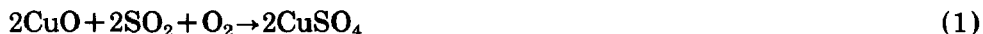
LITERATURE REVIEW

In previous studies on CuO processes and related kinetics, predominantly impregnated CuO on γ -alumina sorbents were tested with a Cu weight fraction of 5–10% [4,14,15].

The question of the optimum copper content was discussed by McCrea et al [4]. They reported for a γ -alumina support that more than 4–6 wt-% of copper led to a decrease of the SO_2 absorption rate probably due to a decreased porosity of the sorbent. A copper content lower than 4–6 wt-% also gave a lower absorption rate, which was ascribed to an incomplete coverage of the internal surface area.

Sulphation

Although the mechanism of the reaction between sulphur dioxide and supported CuO under flue gas conditions remained unclear, there is general agreement about the overall reaction taking place in the temperature range of 300–450°C



Small quantities of sulphur trioxide (SO_3) present in flue gas react with CuO to CuSO_4 as well (generally SO_3 comprises 1% of the SO_x total in flue gas) Copper sulphite (CuSO_3) is thermodynamically unstable in an oxidising atmosphere [16] Kent et al [17] confirmed experimentally that there is no formation of copper sulphite when oxygen is present. At higher temperatures sulphation remains incomplete due to the reverse reaction and to partial decomposition of the sulphate formed to CuO and SO_3 McCrea et al [4] reported this to start at approximately 450°C for CuO supported on γ -alumina Above 700°C, no copper sulphate was formed at all They also measured that the γ -alumina support itself was sulphated to approximately 1–2 wt-% Sulphation of the γ -alumina support was also mentioned by Princiotta et al [18]

Several papers report on kinetic studies of the sulphation reaction Yeh et al [19] as well as Vogel et al [20] found the intrinsic reaction rate of the sulphation of CuO supported on γ -alumina to be directly proportional to the SO_2 concentration in the gas phase and to the fraction of unreacted CuO In case of flue gas conditions the sulphation rate is generally measured to be independent of the oxygen concentration because in flue gas there is a large excess of oxygen when compared to sulphur dioxide

Laguerie and Barreteau [21] studied SO_2 absorption on an alumina-supported CuO sorbent in a counterflow multistage fluidised bed reactor They found no influence of the NO_2 concentration (between 0 and 150 ppm) while the presence of 11–17% carbon dioxide led to a slight decrease in SO_2 absorption degree compared to experiments without any carbon dioxide in the simulated flue gas Variation of the water vapour concentration between 2 and 20% was determined to have a considerable effect on the SO_2 absorption degree A maximum in the SO_2 absorption degree occurred between 6 and 10% for SO_2 inlet concentrations of 2000–4000 ppm and a bed temperature of approximately 300°C For an SO_2 inlet concentration of 1000 ppm the maximum was absent, the SO_2 absorption degree decreased continuously with increasing water vapour content of the simulated flue gas

Data on the influence of temperature on the sulphation kinetics are rather scarce Deberry and Sladek [16] reported an activation energy of 112 kJ/mol for pure CuO, determined from microbalance experiments. Yeh et al [19] also

conducted microbalance experiments, but they tested a CuO on γ -alumina sorbent (5.6 wt-% Cu) and found a much lower activation energy of 20.1 kJ/mol

Reduction of the sulphated sorbent

It is possible to regenerate the sulphated sorbent by thermal decomposition at about 700°C. However, this regeneration is slow and leads to loss of absorptive activity and mechanical strength [4]. Therefore reductive regeneration is generally proposed, using (mixtures of) hydrogen, carbon monoxide or methane as a reducing gas.

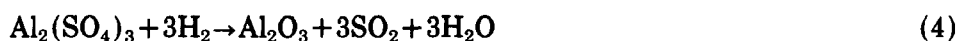
Hydrogen

Reduction of pure CuSO₄ by hydrogen proceeds rapidly above 200–250°C, mainly according to the overall reaction



Vo Van and Habashi [22,23] and Jacinto et al [24] studied the reduction by hydrogen of pure unsupported CuSO₄. Below 400°C, they found the reduction to proceed according to reaction (2) with copper(I) sulphate as an intermediate. SO₂ and H₂O were the only gaseous reaction products. Jacinto et al [24] also conducted experiments above 400°C and they found that up to 560°C reaction (2) is the overall reaction. However, when temperatures were increased Cu₂O instead of Cu₂SO₄ became increasingly important as an intermediate product.

Several side-reactions have been reported for the reduction of sulphated CuO-on-alumina sorbents by hydrogen. The most important are



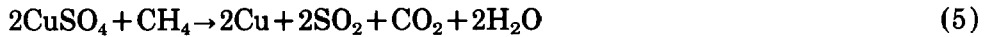
The formation of copper(I) sulphide was predicted by Jacinto et al [24] on the basis of thermodynamic calculations, but they could not detect it upon reducing unsupported copper sulphate. However, Dautzenberg et al [3] reported this reaction to be the most important side-reaction in the SFGT process, where CuO on γ -alumina was used at about 400°C. Up to 33% of the copper sulphate was reduced by this reaction. According to Princiotta et al [18], the formation of copper(I) sulphide in the SFGT process increases with decreasing reduction temperature below 400°C. Reaction (3) is undesirable because (part of the) Cu₂S is oxidised to CuSO₄ when it is contacted with flue gas again [1]. This means that the capacity of the sorbent for SO₂ absorption is reduced, while the consumption of hydrogen is increased.

If the alumina support is partially sulphated during SO₂ absorption, the aluminium sulphate may also be reduced by hydrogen. Habashi et al [25] found for pure aluminium sulphate that below 500 °C no reduction occurred. At higher temperatures the reduction proceeded according to reaction (4) For the SFGT process, Princiotta et al [18] reported the reduction of aluminium sulphate to start at temperatures above 400 °C

For pure CuSO₄, the kinetics of the reduction by hydrogen have been studied by Vo Van and Habashi [23] They measured an activation energy of 62–70 kJ/mol Similar to the case of the sulphation reaction, Yeh et al [19] found a much lower activation energy (11.5 kJ/mol) for CuSO₄ on γ -alumina They also determined the reaction rate to be first order in the hydrogen concentration

Methane

It is also possible to regenerate the sulphated sorbent with methane according to the overall reaction



At the temperature level appropriate for SO₂ absorption, the reduction by methane is much slower than the reduction by hydrogen [3,19] McCrea et al [4] found for an impregnated CuO-on-alumina sorbent that the methane consumption during reduction is in agreement with reaction (5) They concluded that side-reactions were less prominent than for the reduction by hydrogen This has also been reported by Princiotta et al [18]

Yeh et al [19] determined an activation energy of 108.6 kJ/mol and a first order dependence with respect to the methane concentration for the reduction of a CuO-on-alumina sorbent with methane

Other reducing agents

Besides hydrogen and methane, carbon monoxide and higher hydrocarbons can also be used as reducing agents Especially mixtures of hydrogen and carbon monoxide, prepared by steam-reforming of natural gas or by coal gasification, may be interesting from an economic point of view According to Princiotta et al. [18], higher hydrocarbons tend to leave coke-like deposits on the sorbents These will be readily burnt off during oxidation, but this may cause high particle temperatures

Oxidation of the reduced sorbent

In a CuO desulphurisation process, the oxidation generally takes place when the reduced sorbent is contacted again with the flue gas [3,5] Metallic copper is then rapidly oxidised to CuO The possibly present intermediate products of the reduction, Cu₂SO₄ and Cu₂O, are oxidised to CuSO₄ and CuO respectively

at temperatures above 200°C [22] Ploeg [1] reported, as mentioned above, that Cu_2S is oxidised to CuSO_4 and CuO at 400–500°C



He also mentioned that approximately half of the sulphur bound as sulphide was liberated as sulphur dioxide during the oxidation, according to:



EXPERIMENTAL

Sorbent preparation

To meet the special demands set by the conditions in a gas–solid trickle flow absorber, two silica-supported CuO sorbents were developed and prepared by Van der Grift and co-workers at the Department of Inorganic Chemistry of the University of Utrecht. The supports of these sorbents were manufactured by Shell according to a sol-gel technique [10]. For the two sorbents, a “narrow pore” (np) and a “wide pore” (wp) support were applied with an average pore diameter of 15 nm and 60 nm respectively. Physical properties of the supports are given in Table 1.

An ion-exchange technique was applied to create a uniform, highly dispersed

TABLE 1

Properties of the silica-supported CuO sorbents investigated

| sorbent ^a | np(5 7)/ np(11 9) | wp(4 5)/ wp(6 1) | im(3 0)/ im(14 0) | pr(4 7) ^b / pr(17 4) |
|---|----------------------|---------------------|----------------------|------------------------------------|
| Support | sol-gel (Shell) | sol-gel (Shell) | sol-gel | aerosil 380V (Degussa) |
| Average particle dia (mm) | 1.5 | 1.5 | 0.65 | 0.25 |
| Average pore dia (nm) | 15 | 60 | 24 | – |
| Pore volume (ml/g) | 1.0 | 1.0 | – | – |
| Internal surface area (m ² /g) | ~265 | ~65 | 180 | 230 |
| Apparent density (kg/m ³) | 700 | 700 | – | – |
| CuO -deposition technique | ion-exchange | ion-exchange | impregnation | dep-precipitation |
| Deposit size (nm) | – | – | 20–50 | 2–5 |
| Cu-content (wt-% of oxidised sorbent) | 5.7/11.9 | 4.5/6.1 | 3.0/14.0 | 4.7/17.4 |

^aAll the sorbents were developed and prepared by Van der Grift and co-workers (see ref. 9), except the np(5 7) and wp(6 1) sorbents which were prepared by Engelhard Co. (The Netherlands)

^bThese sorbents are equal to the CuU05 and CuU20 sorbents described by Van der Grift et al. [13]

CuO deposition [12] Concentrated ammonia was added to an aqueous solution of copper nitrate $[\text{Cu}(\text{NO}_3)_2]$ After redissolution of precipitated basic copper nitrate as copper(II) tetramine, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, the solution was replenished with 0.1 M ammonia buffer of pH 10 to limit pH changes during the preparation The silica spheres were suspended in this continuously stirred $[\text{Cu}(\text{NH}_3)_4]^{2+}$ solution (25 mM) at room temperature Subsequently, the loaded silica spheres were dried and calcined at 450°C The silica spheres were subjected to three cycles of ion-exchange, drying and calcination to achieve a sufficiently high copper oxide loading The two thus prepared, ion-exchanged sorbents are coded np(11.9) and wp(4.5), with the weight percentage of Cu given in parentheses

Two similar ion-exchanged sorbent batches were prepared by Engelhard in quantities sufficient for application in a bench-scale plant [8] One of these ion-exchanged sorbents, coded wp(6.1), was prepared by a threefold ion-exchange on a wide pore support as described above, while the other, coded np(5.7), consisted of a narrow pore support, which underwent the ion-exchange, drying and calcination cycle just once

The four batches of ion-exchanged sorbents were ground and sieved, and the size-fraction with a particle diameter of 150–300 μm was used for the microbalance experiments

In addition, four silica-supported sorbents were prepared by two other techniques, viz vacuum impregnation and homogeneous deposition-precipitation [12,13] The support of these sorbents was not optimised for application in the new continuous flue gas treating process with a gas–solid trickle flow absorber

First, vacuum impregnation with a $\text{Cu}(\text{NO}_3)_2$ solution was used for the preparation of two sorbents with different copper contents, im(3.0) and im(14.0) The support consisted of porous silica spheres, which were prepared by a sol-gel technique For the experiments in the microbalance, sorbent spheres with a diameter of 500–800 μm were used

Secondly, two sorbents, pr(4.7) and pr(17.4), were prepared by homogeneous deposition-precipitation These sorbents are equal to the sorbents coded CuU05 and CuU20 respectively in [13]. The particle diameter of these sorbents was 150–300 μm

For the two ion-exchanged sorbents prepared by Engelhard for bench-scale testing [np(5.7) and wp(6.1)], the copper content given in parentheses was determined by chemical analysis The copper content indicated for the other six sorbents prepared by Van der Grift and co-workers was determined from the last sulphation run of the standard test (see section "Apparatus and experimental methods"), assuming only the conversion of CuO to CuSO_4 to occur [reaction (1)] These values represent the weight percentage of copper (in the oxidised sorbent), which is actually taking part in the sulphation–regeneration cycles Compared to the "total" copper content obtained by chemical

in the centre of the reactor section. A chromel–alumel thermocouple was placed at the same height as the sample pan in a quartz capillary inside, and near the wall of the hang down tube to determine the reaction temperature. In a separate experiment, the temperature in the centre of the hang down tube was measured and found to be equal to the temperature in the capillary.

The composition of the gas mixtures was adjusted by Brooks mass flow controllers. The total flow rate of the gas was approximately $3.3 \cdot 10^{-6} \text{ m}^3/\text{s}$ (at 0°C and atmospheric pressure). Water vapour was added to the gas mixture by two bubblers in series, which were placed in a thermostated bath (6). All the gas supply tubing after the thermostated bath was kept at a temperature of about 80°C to prevent condensation of the water vapour. Before entering the reactor tube, the gas mixture was preheated in a quartz tube, which was filled with 2 mm diameter glass beads and placed in a second tubular furnace (5).

In experiments meant to realise simultaneous oxidation and sulphation of the reduced sorbent, oxygen and sulphur dioxide were premixed. To minimise the residence time distribution in the supply tubing for both gases, the O_2/SO_2 supply was purged using the three-way valve (7), until an experiment was started.

The external mass transfer rate from the bulk of the gas phase to the sorbent particles in the sample pan was determined by sublimation of naphthalene [26]. Experimentally observed rates of sulphation and reduction could then be corrected for the influence of external mass transfer. The maximum correction was 10%. To determine whether the reaction rates were influenced by pore diffusion, some experiments were carried out using particles with a diameter of 44–53 μm instead of 150–300 μm . The reaction rates observed in these experiments were equal to those from experiments with the larger particles. Therefore the influence of pore diffusion on the reaction rate must be negligible.

From a simple heat balance, the exothermic sulphation and reduction were estimated to cause a maximum increase of sorbent-sample temperature increase of approximately 2°C for the experimental conditions applied, which was neglected. The temperature effect of the exothermic oxidation (estimated maximum temperature increase 10°C) is discussed in detail on p. 30.

To allow a correct comparison of the different sorbents, a standard test procedure was developed. According to this procedure, the sorbents were first calcined for three hours in nitrogen at a temperature of 370°C . Then, at the same temperature, they were subjected to three cycles of (i) complete reduction by hydrogen (until a constant weight level was reached), (ii) quenching with nitrogen, (iii) oxidation (10 min), (iv) sulphation (60 min) and (v) quenching with nitrogen again. Subsequently, the temperature was raised to 445°C and the sorbents were reduced by methane. The final oxidation and sulphation steps were then carried out at 370°C again. To achieve complete sulphation of

TABLE 2

Standard experimental conditions

*Reactor temperature*370 °C for oxidation, sulphation, and reduction by H₂445 °C for reduction by CH₄*Gas mixtures*

| | |
|------------------------------|---|
| Oxidation | 5.0% O ₂ , 10.4% H ₂ O, balance N ₂ |
| Sulphation | 0.2% SO ₂ , 5.0% O ₂ , 10.0% H ₂ O, balance N ₂ |
| Reduction (H ₂) | 18.0% H ₂ , 10.4% H ₂ O, balance N ₂ |
| Reduction (CH ₄) | 45.0% CH ₄ , 10.4% H ₂ O, balance N ₂ |
| Quenching | 10.4% H ₂ O, balance N ₂ |

the active CuO, the SO₂ concentration was raised from 0.2 to 1.0 vol.-% at the end of the last sulphation.

The composition of the gas mixtures used in these standard tests is given in Table 2. Carbon dioxide was not added to the standard simulated flue gas mixture, because in some separate experiments for the wp(4.5) and wp(6.1) sorbents the presence of 15 vol.-% of carbon dioxide in the simulated flue gas was shown to have no influence on the sulphation rate observed. Experiments with 10% water vapour in the simulated flue gas, however, showed a considerably higher sulphation rate in agreement with the findings of Laguerie and Barre-teau [21] for an alumina-supported CuO sorbent (see section on Sulphation). Therefore, all further experiments were carried out with about 10% water vapour in the gas, which is a normal concentration in flue gases from oil and coal-fired boilers. Water vapour was added to the reducing gas mixture as well, because in a full-size plant steam will be applied as an inert gas. The water vapour concentration in the reducing gas mixture was chosen in such a way that the set-point temperature of the thermostated bath need not be changed during a test cycle.

RESULTS AND DISCUSSION

Side-reactions

For a proper interpretation of the microbalance experiments, e.g. to enable calculation of the amount of SO₂ absorbed during sulphation, it is necessary to determine to what extent side-reactions affect the results of measurements. Therefore, the possibility of reactions between the support and various gaseous components was investigated for a wide pore support (without CuO). In three subsequent cycles of reduction by hydrogen, oxidation and sulphation under the aforementioned standard test conditions (see Table 2) no weight changes were detected. Therefore, the wide pore support may be regarded as an inert

material for the present conditions. The other silica supports used in this study were assumed to be inert as well.

In the standard tests with the silica-supported sorbents, the total weight gain during the oxidation step may give an indication of the amount of copper sulphide formed during the preceding hydrogen reduction step. For np(5.7) and wp(6.1), this weight gain was usually 10–25% larger than expected if only copper were present at the beginning of the oxidation step. This extra weight gain can be explained by assuming that 7 to 17% of the total amount of copper was present as Cu_2S and that it reacted according to reaction (6) during the oxidation. The consequences of such an extent of Cu_2S formation during the hydrogen reduction step for the interpretation of the weight changes during sulphation and reduction are limited. For instance according to the stoichiometry of reaction (6), 3.5–8.5% of the copper would then be present as CuSO_4 at the beginning of the sulphation, and the total weight loss during reduction after complete sulphation would only be about 1–3% smaller than without any Cu_2S formed.

In the following sections, the weight changes during sulphation and regeneration will generally be interpreted as being caused by the main reactions (1) and either (2) or (5).

Conversion behaviour of different silica-supported CuO sorbents

Based on the results of the standard test procedure, the sulphation and regeneration behaviour of the four ion-exchanged sorbents developed especially for the present flue gas treating process with a gas–solid trickle flow absorber was compared to the performance of the four other sorbents prepared by impregnation or homogeneous deposition–precipitation.

Sulphation

In Fig. 2, the weight gain during sulphation under standard test conditions is plotted versus the reaction time, for six of the sorbents tested. If curves of similarly prepared sorbents are compared, a sorbent with a larger copper content shows a larger weight gain after a certain reaction time, i.e. it has a higher sulphation activity. This is in contrast with the results of McCrea et al. [4], who reported a decrease of the sulphation activity for copper contents larger than 4–6 wt-%. The different results are probably explained by differences in internal pore structure, but unfortunately McCrea et al. did not specify the pore structure of their sorbents.

Differences in sulphation activity per unit copper content are represented by the slopes of the curves plotted in Fig. 3. Again, sorbents prepared by the same technique but with a different copper content can be compared. For each type, whether prepared by ion-exchange (np), homogeneous deposition–precipitation (pr) or vacuum impregnation (im), it shows that the sulphation

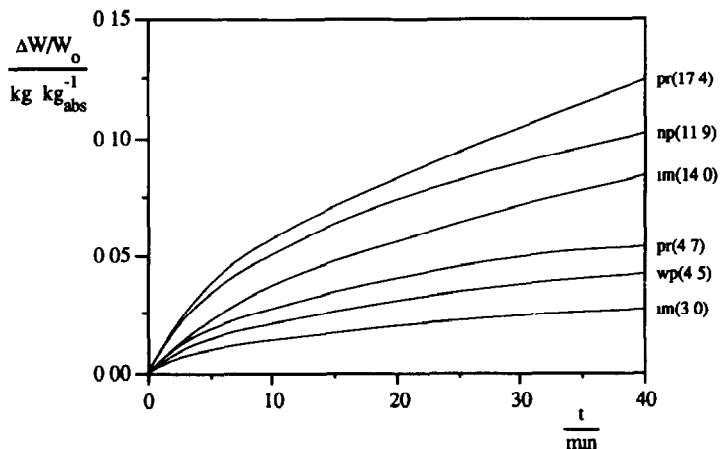


Fig 2 Relative weight gain $\Delta W/W_0$ versus time during sulphation

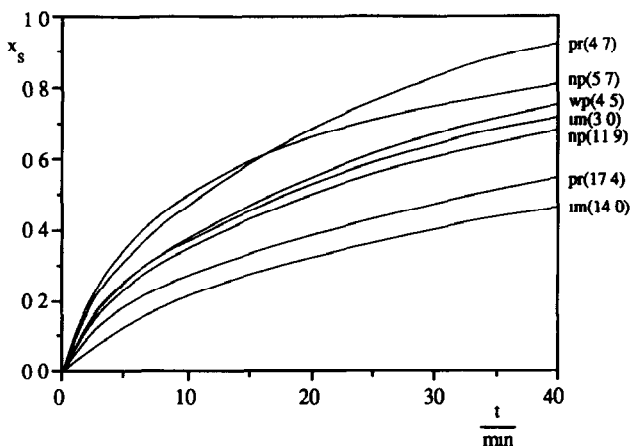


Fig 3 Fractional conversion x_s versus time during sulphation

activity per unit copper content is lower if the copper content is larger. This is probably due to a larger size of the CuO deposits for the sorbents with a larger copper content. An increase of the deposit size with an increasing copper content was confirmed by Van der Grift et al [13] for the pr-sorbents. By using transmission electron microscopy they determined a copper deposit size in the reduced sorbent of 2.3–2.7 nm and 3.5–5.0 nm for the pr(4.7) and pr(17.4) sorbent, respectively. As expected, the im-sorbents with large CuO deposits show a relatively low sulphation activity per unit copper content, while this activity is relatively high for the pr-sorbents with the CuO dispersed very well on a large internal surface area.

The np(11.9) and wp(4.5) ion-exchanged sorbents have an intermediate

sulphation activity per unit copper content. The CuO seems to be slightly better dispersed on the wp(4.5) sorbent, because it shows a higher sulphation activity per unit copper content, although the total copper content per unit internal surface area is higher.

Reduction by hydrogen

Typical reduction degree (x_r) versus time (t) plots for the reduction by hydrogen of the previously sulphated sorbents are given in Fig 4. In Fig 4a, the curve is clearly S-shaped. This shape is characteristic of an autocatalytic gas-solid reaction. An autocatalytic reaction is generally divided into three stages: induction, acceleration (the autocatalytic stage) and decay (decreasing rate). During the induction stage, the reaction starts at separate, more active sites and seeds or islands of solid reaction product are formed. Thereupon the reaction proceeds rapidly at the interface between these islands and the unreacted part of the solid during the acceleration stage, while being catalysed by the solid reaction product. In fact, the reaction rate increases due to an increase of this interfacial area. Finally, during the stage of decay, the islands become interconnected, which leads to a decrease in interfacial area and consequently to a decreasing reaction rate.

The reduction by hydrogen of (supported) CuO is a well-known autocatalytic reaction, which has been studied extensively in relation to the use of copper catalysts for low-temperature hydrogenation processes, as well as for the oxidation of carbon monoxide and organic compounds [27,28]. However, to our knowledge the reduction by hydrogen of (supported) CuSO₄ has not yet been identified as an autocatalytic reaction. For instance, in the study of Yeh et al. [19] a model was used instead, in which the reduction was taken to be n -th order in the fraction of unreacted CuSO₄. This approach can be understood by considering the result for the impregnated sorbent im(3.0) in Fig 4b. Here, just as in ref. 19, a considerable tailing tends to conceal the S-shape of the curve. If the fractional reduction rate is presented as a function of the

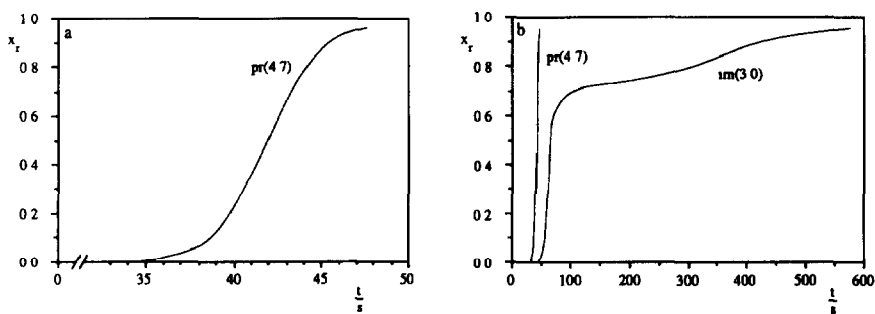


Fig 4 Typical reduction degree (x_r) versus time (t) plots for regeneration by hydrogen

reduction degree, however, the characteristics of an autocatalytic reaction appear again in the form of a curve with a parabolic shape (see Fig. 5)

Voge and Atkins [27], who studied the reduction by hydrogen of different supported CuO catalysts, also found this tailing for several of their catalysts and ascribed it to a strong interaction between part of the CuO and the support. We found the considerable tailing only for the impregnated sorbents. Yet there seems no essential difference in CuSO₄-support interaction between these sorbents and the sorbents prepared by homogeneous deposition-precipitation. It is more likely that the tailing for the impregnated sorbents was due to the large size of the copper deposits. Apparently, after a certain reduction degree the

TABLE 3

Values of parameters characterising the reduction for the sulphated sorbents under standard test conditions (see Table 2), and at two other temperatures for the wp(6 1) sorbent

| | | $t_{0.05}$ (s) | $(dx_r/dt)_{\max}$ (s ⁻¹) | $t_{0.90}$ (s) |
|------------------------------|-------|-------------------|--|-------------------|
| <i>Reduction by hydrogen</i> | | | | |
| np(5 7) | | 47 | 0.113 | ~70 |
| wp(6 1) | 370°C | 49 | 0.086 | ~70 |
| | 332°C | 111 | 0.052 | - |
| | 293°C | 375 | 0.014 | - |
| pr(4 7) | | 38 | 0.160 | 45 |
| im(3 0) | | 54 | 0.054 | 420 |
| <i>Reduction by methane</i> | | | | |
| np(5 7) | | 216 | 0.0010 | - |
| wp(6 1) | | 54 | 0.0013 | 1350 |
| pr(4 7) | | 100 | 0.00086 | 2400 |
| pr(17 4) | | 480 | 0.00046 | 3100 |
| im(3 0) | | 170 | 0.00021 | - |

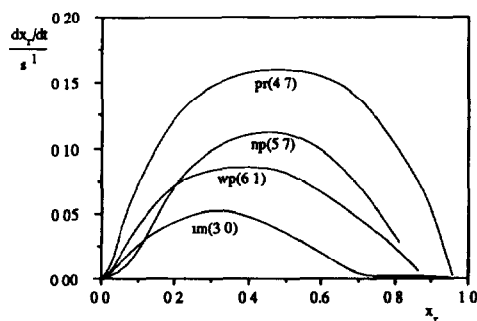


Fig 5 Fractional reduction rate versus reduction degree for regeneration by hydrogen

reduction rate collapses due to severe transport limitations inside the large copper deposits

Besides the S-shape and tailing of the curve, a remarkable phenomenon illustrated by Fig 4 is the relatively long induction period In Fig. 4a, the induction period amounts to about 38 s, while over 90% of the reduction occurs within the next 10 s

Because of this long induction period, the S-shaped curve and the possible tailing, it seems most appropriate for design purposes to characterise the reduction by using three parameters (i) the time required for 5% conversion, (ii) the maximum conversion rate, and (iii) the time needed for 90% conversion The percentages 5 and 90% have been chosen arbitrarily For several sorbents investigated, values of these parameters for the reduction of the sulphated sorbent by hydrogen under standard test conditions are given in Table 3 Together with Fig. 5 this table illustrates that the reduction by hydrogen of the ion-exchanged sorbents is similar to the reduction of the deposition-precipitated sorbents; it only proceeds at a somewhat lower rate The absence of tailing and the S-shape of the x_r, t -curve favour a kinetic model based on a single overall reaction instead of two (or more) consecutive reactions with an intermediate product

Reduction by methane

The reduction of previously sulphated sorbents by 45% methane at 445 °C differs in several ways from the reduction by 18% hydrogen at 370 °C As can be seen from comparing Figs 6 and 7 with 4 and 5 respectively, the reduction by methane is much slower despite the higher temperature and the higher concentration Besides, the shape of the x_r, t -curves is somewhat different Instead of a single S-shape, as was found for the reduction by hydrogen (see Fig 4) the

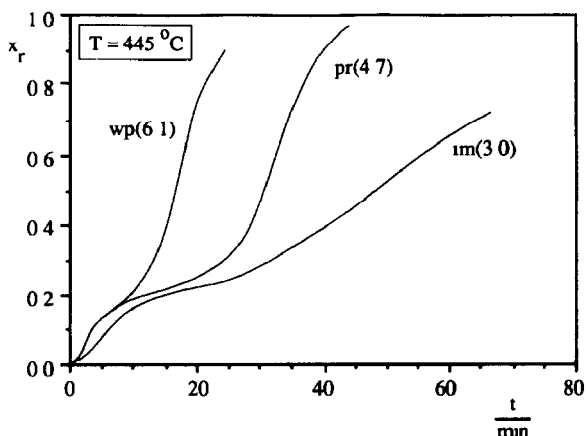


Fig 6 Typical reduction degree versus time plots for regeneration by methane

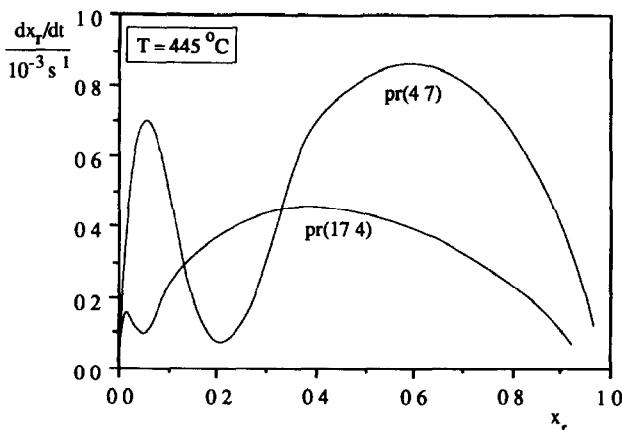


Fig 7 Influence of copper-weight percentage on the fractional reduction rate for the regeneration by methane of the sorbents prepared by homogeneous deposition-precipitation

x_r, t -curves of the reduction by methane (Fig 6) show a double S-shape. The fractional reduction rate, that is the gradient of the x_r, t -curve, has two maxima with a minimum located in between. In Fig 7, the fractional reduction rate is plotted versus the reduction degree for two previously sulphated sorbents prepared by homogeneous deposition-precipitation. Clearly, the relative importance of the first maximum decreases with increasing copper content of the sorbent (the reduction degree x_r , for which the minimum occurs, is about 4 times higher for the pr(4.7) than for the pr(17.4) sorbent).

In Table 3, the reduction of several previously sulphated sorbents by methane is characterised by the same parameters as the reduction by hydrogen. Just as in the case of reduction by hydrogen, the deposition-precipitated sorbents pr(4.7) and pr(17.4) show a much higher maximum fractional reduction rate than the impregnated sorbent im(3.0). It remains unclear, however, whether the impregnated sorbent exhibits a considerable tailing for the reduction by methane as well, because the previous sulphation was not carried out completely. Surprisingly, the maximum rates for the ion-exchanged sorbents do not range between the maximum rates for the pr(4.7) and im(3.0) sorbents as it was found for the reduction by hydrogen. Instead, they are even higher than the maximum rate for the pr(4.7) sorbent.

Reaction kinetics for two ion-exchanged sorbents prepared for bench-scale testing

The reaction kinetics of regenerative SO_2 absorption were studied in detail for the two ion-exchanged sorbents, coded np(5.7) and wp(6.1), which were prepared by Engelhard for bench-scale testing.

Sulphation

Generally, the intrinsic reaction rate for the sulphation can be expressed as a function of the reaction temperature T , the oxygen concentration C_{O_2} , the sulphur dioxide concentration C_{SO_2} and the sulphation degree x_s ,

$$r = \frac{\zeta \rho_s}{M_{Cu}} \frac{dx_s}{dt} = k_0 \exp(-E_a/RT) C_{O_2}^m C_{SO_2}^n F(x_s) \quad (\text{mol m}_{\text{abs}}^{-3} \text{s}^{-1}) \quad (8)$$

As mentioned on p 22, the sulphation rate is not influenced by the carbon dioxide concentration in the (simulated) flue gas. The water vapour concentration does affect the sulphation rate, but was not introduced into this rate equation, because it was kept at a constant level of 10% in all the experiments.

For the function $F(x_s)$, the following form is usually applied in literature [16,19]

$$F(x_s) = (1 - x_s)^p \quad (9)$$

where p is the order of the reaction with respect to the unreacted CuO.

To determine whether the generally found first order ($p=1$) also applies for the np(5.7) and wp(6.1) sorbents, the fractional sulphation rate dx_s/dt is plotted versus the sulphation degree x_s in Fig. 8. For comparison, experimental results obtained for two sorbents prepared by impregnation [im(3.0)] and deposition-precipitation [pr(4.7)] are presented as well. The approximately straight lines in Fig. 8, extending over $0.1 < x_s < 0.9$ and referring to the ion-exchanged sorbents and the pr(4.7) sorbent, indicate the sulphation rate to be first order in the fraction of unreacted CuO indeed. Initially, however, that is for $x_s < 0.1$ [or $x_s < 0.3$ in case of the im(3.0) sorbent], a much

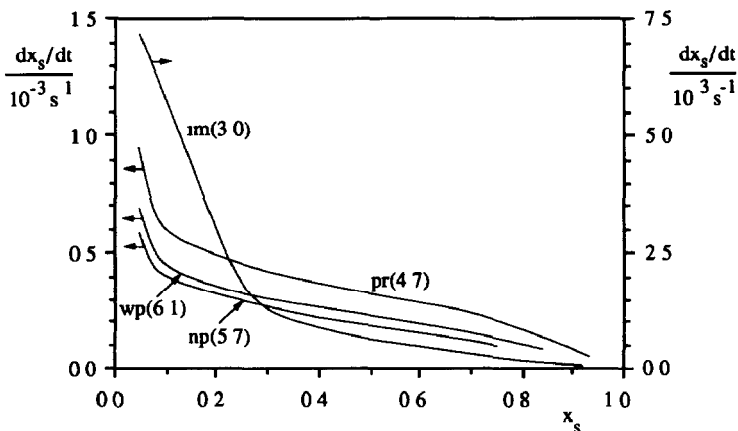


Fig. 8 Conversion rate versus fractional conversion during sulphation. Standard conditions were used (e.g. 0.2 vol.-% SO_2 , see Table 2) except for the experiment with the im(3.0) sorbent, where the SO_2 concentration was 1 vol.-%.

stronger dependence was observed, Literature data of Yeh et al [19] and Vogel et al [20] also reveal such a stronger than first order dependence

This initially stronger dependence is possibly due to the following phenomenon. If, despite a long pre-oxidation period (10 min in our experiments), the oxidation of copper to CuO is still not complete at the start of the sulphation, then the copper deposits may consist of an unreacted copper core with a surrounding dense CuO layer. Upon sulphation, this CuO is converted to CuSO₄. Because the molar volume of CuSO₄ is much larger than that of CuO (CuSO₄ 44.3 cm³/mol, CuO 12.4 cm³/mol [29]), the exterior structure of a deposit would be changed in a way that the internal copper core becomes easily accessible to the gaseous reactants SO₂ and O₂. Then, the relatively fast oxidation occurs simultaneously, next to the sulphation, causing an extra weight gain of the sorbent sample. That this effect is strongest for the impregnated sorbent, i.e. high sulphation rates up to a relatively high sulphation degree $x_s=0.3$, seems in agreement with this explanation, because the copper deposits are largest for this sorbent.

For general design purposes, it is sufficiently accurate to assume a first order dependence ($p=1$) over the entire conversion range for both the np(5.7) and wp(6.1) ion-exchanged sorbents.

The values of the other parameters of the intrinsic rate equation (8), viz k_o , E_a , n and m , were determined for both ion-exchanged sorbents by a systematic variation of the reaction temperature (327–407°C), the SO₂ concentration (0.05–0.40 vol.-%) and the oxygen concentration (1.0–10.0 vol.-%) respectively, while maintaining the other conditions as indicated for the standard test (see Table 2). The sorbents were reduced by hydrogen and pre-oxidation was carried out for 14 min. To minimise experimentation time, the sulphation was stopped at a sulphation degree of approximately $x_s=0.40$.

During these experiments, the sorbent samples showed some loss of activity in the first 1 to 3 cycles of sulphation, reduction and oxidation. However, in the following cycles, up to a number of 75, no further deactivation occurred. For sulphation degrees of $0.1 \leq x_s \leq 0.4$, the sulphation was found to be first-order with respect to the SO₂ concentration ($n=1$) and independent of the oxygen concentration ($m=0$) for both sorbents, which is in agreement with literature data of alumina-supported CuO sorbents. The Arrhenius plots showed straight lines for the temperature range investigated (327–407°C), and the following values were determined for the activation energy E_a and the frequency factor k_o : np(5.7) $E_a=86$ kJ/mol, $k_o=6.6 \cdot 10^7$ s⁻¹, and wp(6.1) $E_a=103$ kJ/mol, $k_o=1.9 \cdot 10^9$ s⁻¹.

The activation energies are much higher than determined by Yeh et al [19] for CuO on a γ -alumina support ($E_a=20.1$ kJ/mol), but somewhat lower than the value found by DeBerry and Sladek [16] for pure CuO ($E_a=112$ kJ/mol).

The difference in activation energy between the np(5.7) and the wp(6.1) sorbent might be explained by the difference in preparation procedure. The

np(5 7) sorbent underwent the ion-exchange absorption cycle only once, while three cycles were applied to prepare the wp(6 1) sorbent. Probably, this resulted in larger and more homogeneous CuO deposits for the latter sorbent.

Now that all the parameters of eqn (8) are known, the sulphation rate can be calculated for every experimental condition within the ranges investigated. Yeh et al [19] presented the following rate equation for the sulphation of their CuO-on-alumina sorbent:

$$\frac{dx_s}{dt} = k_o \exp(-E_a/RT) P_{SO_2} (1 - x_s) \quad (10)$$

with $k_o = 13.06 \text{ s}^{-1}$ and $E_a = 20.1 \text{ kJ/mol}$. At 350°C , the presently observed fractional sulphation rates for the np(5 7) and wp(6.1) sorbents are approximately 50% lower than predicted by eqn (10). On the other hand, they are slightly higher at 400°C due to the higher activation energies of both ion-exchanged sorbents.

Reduction by hydrogen

The kinetics of the reduction by hydrogen after complete sulphation have, to a limited extent, been further characterised for the wp(6 1) ion-exchanged sorbent. Results of an experiment with 1.4% hydrogen instead of 18% suggest that the reduction is first order with respect to the hydrogen concentration, which is in agreement with literature data for a γ -alumina supported CuO sorbent. The influence of temperature on the hydrogen reduction of the sulphated wp(6 1) sorbent is shown in Table 3 and in Fig 9. When the temperature is decreased from 370°C to 293°C , the shape of the x_r, t -curve remains unaltered (S-shape without considerable tailing), but the induction period becomes about 7.5 times longer and the maximum fractional reduction rate about 6 times

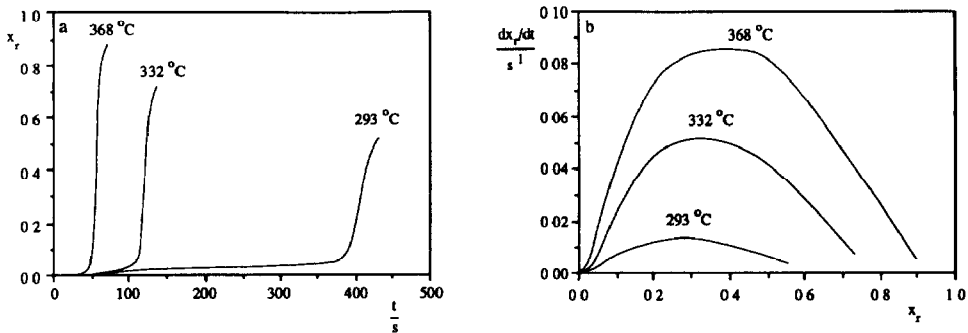


Fig 9 Influence of temperature on regeneration with hydrogen for the ion-exchanged sorbent wp(6 1)

lower. From the values for the maximum fractional reduction rate, an activation energy of $E_a = 74$ kJ/mol can be derived. Just as in the case of the sulphation, this value is much higher than reported by Yeh et al. [19] for their CuO-on-alumina sorbent ($E_a = 11.5$ kJ/mol). But it is quite close to the one determined by Vo Van and Habashi [23] for unsupported copper sulphate (62–70 kJ/mol).

Influence of simultaneous oxidation on the sulphation rate

In studies on the regenerative SO_2 -absorption kinetics of CuO sorbents, the oxidation of the sorbent is generally carried out prior to the sulphation, although in real processes the oxidation and sulphation often occur simultaneously. In most of the present experiments, the sorbents underwent separate pre-oxidation as well. However, in some additional experiments the influence of simultaneous oxidation on the sulphation rate was examined.

If oxidation is carried out simultaneously, the weight gain is caused by two simultaneous reactions, viz. oxidation and sulphation. For a correct comparison between the sulphation rates with and without simultaneous oxidation, it should be known which part of the weight gain is caused by sulphation in case of simultaneous oxidation. This cannot be calculated exactly, because a priori the relative rates of both reactions are unknown. However, a minimum and a maximum for the SO_2 absorption can be determined based on two extreme scenarios.

In the first scenario, it is assumed that each copper atom is converted to CuSO_4 in one step. The oxidation and sulphation then proceed at an equal rate. If the oxidation is faster than the sulphation, which is generally found, then initially the fraction of the weight gain due to SO_2 absorption is smaller than according to this scenario. Therefore, this scenario sets a maximum for the SO_2 absorption. According to the second scenario, setting a minimum for the SO_2 absorption, the reduced sorbent is first completely oxidised (all copper is converted to CuO) before the sulphation starts. This implies that the rate of oxidation is much larger than the rate of sulphation; the initial weight gain is completely due to oxidation.

It should be noted that the final weight gain caused by the simultaneous oxidation is always taken to be equal to the total experimentally observed weight gain of separate oxidation. This weight gain is 10–25% higher than according to the reaction of Cu to CuO, which may be attributed to the oxidation of some Cu_2S formed during the previous reduction by hydrogen.

Fig. 10 shows the influence of simultaneous oxidation on the SO_2 absorption for the wp(6.1) sorbent. The shaded band represents possible amounts of SO_2 absorbed versus time for the case of simultaneous oxidation, the boundaries of this shaded band are determined by the minimum and maximum scenarios outlined above. It can be seen clearly that, up to about 60% conversion to sulphate, the absorption rate is considerably higher in case of simultaneous oxidation regardless of the assumption for the oxidation rate (for $x_s \leq 0.60$, the

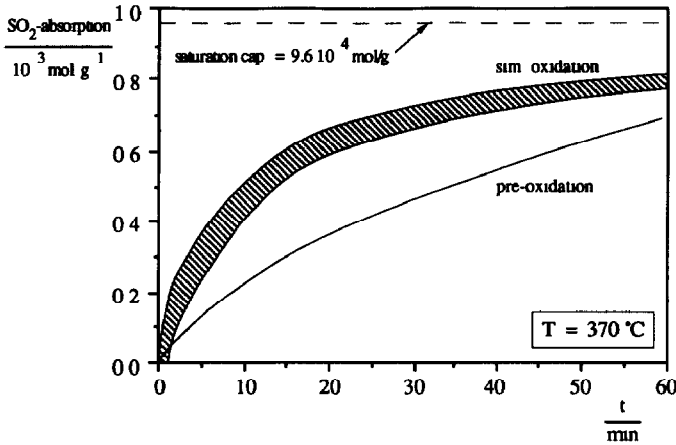


Fig 10 Influence of simultaneous oxidation on SO₂ absorption for the ion-exchanged sorbent wp(6.1)

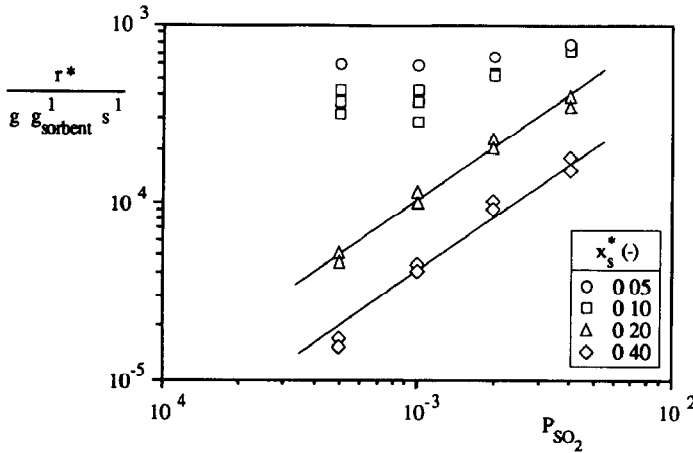


Fig 11 Influence of the SO₂ concentration on the overall reaction rate in case of simultaneous oxidation and sulphation of the ion-exchanged sorbent wp(6.1) The straight lines correspond to a first order dependence with respect to the SO₂ concentration

slope of the shaded-band curves is always larger than the slope of the line obtained for sulphation of pre-oxidised samples)

The experimental results presented in Fig 11 give an indication of which of the two SO₂ absorption limits for the simultaneous oxidation and sulphation is closest to reality The overall reaction rate for the wp(6.1) sorbent, defined as the weight gain (due to combined oxidation and sulphation) per unit of sample weight and per unit of time, is shown as a function of the fractional partial pressure of SO₂ and for various conversion degrees x_s^* The conversion degree x_s^* is defined as the ratio of the actual weight gain and the weight gain

occurring if all the copper would react from Cu to CuSO_4 . It appears that the overall reaction rate is almost independent of the SO_2 concentration for $x_s^* < 0.20$, while for $0.20 \leq x_s^* \leq 0.40$ it is first order with respect to the SO_2 concentration, just as in the case of separate oxidation precedent to sulphation. This was observed for the np(5.7) sorbent as well, and it indicates that in the beginning the weight gain is mainly caused by oxidation, while for $x_s^* \geq 0.20$ sulphation is the main reaction. Also, $x_s^* = 0.20$ roughly corresponds to the conversion level that can be reached if all the copper is (only) oxidised to CuO. Therefore, the true SO_2 absorption during simultaneous oxidation and sulphation is probably closest to the calculated minimum level for both sorbents.

Moreover, this seems to be supported by the activation energy of the overall reaction, which was determined as a function of the fractional conversion for both sorbents in the temperature range 327–407°C. For $0.20 \leq x_s^* \leq 0.40$, the activation energy was found to be equal to that for separate sulphation [86 and 103 kJ/mol for the np(5.7) and wp(6.1) sorbents, respectively], while much lower values were found for $x_s^* = 0.05$ and $x_s^* = 0.10$ [np(5.7). 17 and 26 kJ/mol, and wp(6.1) 10 and 24 kJ/mol, respectively].

The order of the overall reaction with respect to the oxygen concentration was found to be approximately 0.35 for both sorbents and low values of x_s^* . For $x_s^* \geq 0.20$, the influence of the oxygen concentration on the overall reaction rate decreased but did not disappear completely, as was to be expected from the experiments with separate oxidation and sulphation. An order of approximately 0.15 remained for both sorbents in the range of conversion degrees investigated (up to $x_s^* = 0.40$).

In Fig. 12, the fractional sulphation rates under standard conditions (see Table 2) in case of simultaneous oxidation (minimum scenario) and after pre-oxidation are plotted versus the sulphation degree x_s . Up to $x_s = 0.40$, the fractional sulphation rate in case of simultaneous oxidation is about 5 times higher for the np(5.7) sorbent, and about 2 times for the wp(6.1) sorbent, than the rate after pre-oxidation. Beyond $x_s = 0.40$ – 0.60 , the fractional sulphation rate in case of simultaneous oxidation rapidly decreases to values even lower than after pre-oxidation. For $x_s \leq 0.50$, the fractional sulphation rates in case of simultaneous oxidation and sulphation can be approximated by the straight lines in Fig. 12, which have been calculated using the following equations:

$$\text{np}(5.7) \quad \frac{dx_s}{dt} = 6.1 \cdot 10^5 \exp(-86 \cdot 10^3/RT) C_{\text{O}_2}^{0.15} C_{\text{SO}_2} (1 - 1.5x_s) \quad (11a)$$

$$\text{wp}(6.1) \quad \frac{dx_s}{dt} = 7.4 \cdot 10^6 \exp(-103 \cdot 10^3/RT) C_{\text{O}_2}^{0.15} C_{\text{SO}_2} (1 - 1.5x_s) \quad (11b)$$

It seems reasonable to assume that this positive effect of simultaneous oxidation on the sulphation rate is at least partly due to a temperature increase

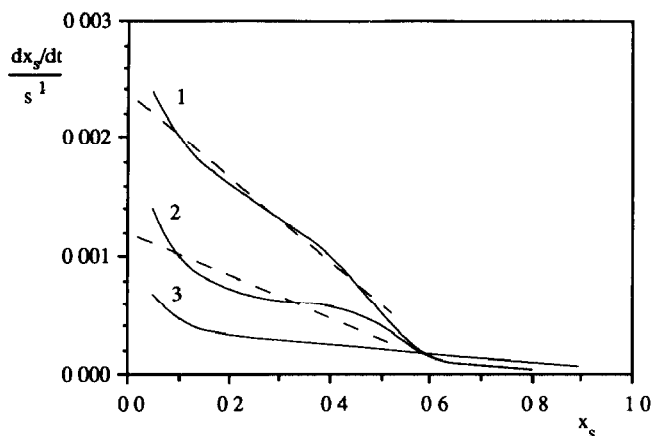


Fig 12 Fractional sulphation rates with simultaneous oxidation (minimum scenario), and with a separate pre-oxidation, versus the sulphation degree x_s . The straight lines represent approximations, calculated according to eqns (11a) and (11b) for the ion-exchanged sorbents np(5 7) and wp(6 1), respectively 1 np(5 7), sim oxidation, 2 wp(6 1) sim oxidation, 3 np(5 7) and wp(6 1) pre-oxidation

of the sample as a result of the exothermic oxidation. Unfortunately, this temperature increase could not be measured in the present experimental set-up. However, a rough estimation of the temperature increase due to the exothermic oxidation reaction can be made based on the following assumptions:

- 1 For the reaction rate, the maximum rate of the overall reaction, that is at $x_s^* = 0$, is taken, it is assumed to be determined by oxidation only.
- 2 Heat transfer occurs only directly from the solids in the sample pan to the gas phase, the heat transfer coefficient can be derived from the mass transfer coefficient by applying the Chilton-Colburn analogy. The mass transfer coefficient was determined experimentally by sublimation of naphthalene.
- 3 There is no temperature gradient in the solids phase.
- 4 The reaction is at steady state.

The temperature increase then follows from a simple heat balance saying that the heat produced by oxidation must be equal to the heat transferred from the solids sample to the gas. For the experimental conditions in this study, a temperature increase of about 10°C was calculated in this way. With the activation energies derived before, this temperature increase would lead to only a 30–35% increase of the sulphation rate at a reactor temperature of 370°C , which is clearly much lower than the 2- and 5-fold increase observed experimentally for the wp(6 1) and np(5 7) sorbents respectively.

Moreover, the experimental results indicate that the oxidation is much faster than the sulphation. Therefore, the temperature increase probably is even lower than 10°C during the major part of the sulphation. This leads to the conclusion that only a small part of the large beneficial effect of simultaneous oxidation

on the sulphation rate can be explained from the accompanying limited temperature increase. Probably, the large beneficial effect is mainly due to structural effects inside the copper deposits. For instance, passivation of the Cu(O) deposits may occur during a long separate pre-oxidation, whereas this possibly is prevented in case of simultaneous oxidation and sulphation due to the combined formation of CuO and CuSO₄. Since a significant temperature effect is estimated not to occur, structural differences also seem to be the reason for the different magnitude of the positive effect of simultaneous oxidation on the sulphation rate for both the wp(6.1) and np(5.7) sorbents

CONCLUSIONS

Major conclusions concerning the kinetics of sulphur dioxide absorption and regeneration of several silica-supported CuO sorbents are

— The reaction kinetics of the ion-exchanged sorbents showed quite close resemblance with the experimental results obtained for the sorbents prepared by homogeneous deposition-precipitation, e.g. a relatively high sulphation activity due to a high dispersion of CuO

— During up to 75 cycles of oxidation, sulphation, and reduction, the ion-exchanged sorbents did not show a significant loss in chemical activity except for some deactivation in the first 1-3 cycles. Furthermore, the undesirable formation of copper sulphide during the reduction by hydrogen seemed to occur only to a small extent and the silica support was found to be inert

— The sulphation kinetics of the pre-oxidised ion-exchanged sorbents are similar to those reported in literature for impregnated alumina-supported CuO sorbents. Under simulated flue gas conditions, the sulphation rate was shown to be first order with respect to the SO₂ concentration and the fraction of unreacted CuO, while no influence of the oxygen concentration was observed. The established activation energies for two different ion-exchanged sorbents were established to be 86 and 103 kJ/mol

— Reduction by hydrogen of the sulphated sorbents was shown to be an autocatalytic reaction. In case of the ion-exchanged sorbents and the sorbents prepared by deposition-precipitation, the time required for complete reduction was mainly determined by a relatively long period of induction. For the impregnated sorbents, on the other hand, the stage of decay appeared to be dominant

— Reduction by methane proceeded much slower than by hydrogen. The S-shape of the conversion versus time curve was observed for methane as well. However, there was no long induction period with a low conversion rate. Instead, the S-shaped part of the curve was preceded by a period with initially a relatively high rate, which subsequently decreased to almost zero

— Experiments, in which the reduced ion-exchanged sorbents were contacted directly with the simulated flue gas, which allows simultaneous oxida-

tion, indicated the oxidation to proceed much faster than the sulphation. This fast simultaneous oxidation was found to have a distinct positive effect on the sulphation rate. The large difference in sulphation behaviour between pre-oxidised and reduced (causing simultaneous oxidation) sorbents was mainly attributed to structural effects inside the CuO deposits.

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NOTATION

| | | |
|-------------------|--|--|
| C | concentration of gaseous reactant | mol m^{-3} |
| E_a | activation energy | J mol^{-1} |
| F | conversion function, see eqns (8) and (9) | |
| k_o | frequency factor | $\text{mol}^{1-m-n} \text{s}^{-1}$ $\text{m}^{-3(1-m-n)}$ |
| k_r | intrinsic reaction rate constant | $\text{mol}^{1-m-n} \text{s}^{-1}$ $\text{m}^{-3(1-m-n)}$ |
| m | order of the reaction with respect to O_2 | |
| M | molecular mass | kg mol^{-1} |
| n | order of the reaction with respect to SO_2 | |
| p | order of the reaction with respect to the fraction of unreacted solid reactant | |
| P_{SO_2} | fractional partial pressure of SO_2 | |
| r | intrinsic reaction rate | $\text{mol m}_{\text{abs}}^{-3} \text{s}^{-1}$ |
| r^* | overall reaction rate | $\text{kg kg}_{\text{abs}}^{-1} \text{s}^{-1}$ |
| R | gas constant | $\text{J mol}^{-1} \text{K}^{-1}$ |
| t | time | s |
| T | temperature | K |
| ΔW | weight change of the sample | kg |
| W_o | initial sample weight | kg_{abs} |
| x_r | fractional reduction of CuSO_4 to Cu | |
| x_s | fractional conversion of CuO to CuSO_4 | |
| x_s^* | fractional conversion of Cu to CuSO_4 | |

Greek symbols

ζ Cu weight fraction of oxidised sorbent

ρ_s apparent density of oxidised sorbent kg m^{-3}

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