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REACTIONS OF SILICA-SUPPORTED COPPER OXIDE AS A REGENERABLE SORBENT FOR FLUE GAS DESULPHURISATION

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ABSTRACT

Silica-supported copper oxide can be used as a regenerable sorbent for flue gas desulphurisation. At 700 K, interaction of sulphur dioxide and molecular oxygen with copper (oxide) leads to the formation of copper sulphate, while upon regeneration of the sorbent metallic copper is formed with simultaneous release of water and sulphur dioxide. The sulphur dioxide present in the flue gas at low concentrations can be trapped and made available at high concentrations by alternating the reaction with copper oxide in the presence of oxygen with the subsequent reduction of the copper sulphate thus formed.

Temperature-programmed sulphation, regeneration and oxidation experiments have been used to study the reactivity of two copper-on-silica sorbents exhibiting different copper particle size distributions. A high dispersion of the copper particles is a prerequisite for a high absorption rate. After a small initial decrease of the SO_2-absorption rate, the CuU20 sorbent containing small silica-supported copper particles shows a stable activity, whereas the CuI20 sorbent containing large copper particles shows hardly any activity for SO_2-absorption.

As demonstrated by XRD, sulphation results in the formation of anhydrous bulk copper sulphate. Upon regeneration, the bulk of the sulphate particles reacts to metallic copper. Measurements of the total hydrogen consumption during regeneration and subsequent temperature-programmed oxidation suggest the retention of sulphur, probably as a surface cuprous sulphide. The retention of sulphur in the regenerated sorbent decreases the absorption rate and the absorption capacity, whereas the consumption of reducing agent is increased. Some reactions are proposed to explain the formation of a surface copper sulphide.

INTRODUCTION

The emission of sulphur dioxide, SO_2, into the atmosphere causes serious air pollution and contributes to the formation of acid rain. Major SO_2-emission sources are power plants burning fossil fuels for electricity generation, refineries and metallurgical installations. Flue gas desulphurisation processes use active sorbents for the removal of SO_2 from the flue gas thus reducing the release of SO_2 into the atmosphere.

Technical desulphurisation processes have to be economically feasible while dealing with the following properties of the flue gas: huge volume

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(space velocity), low SO_2-concentration (0.1–0.5 vol.%), dust (fly ash) and high temperature. Removal of SO_2 from a large volume of flue gas containing dust necessitates requirements concerning the construction of the reactor and the contact between the gas and the sorbent. Ideally, the temperature at which desulphurisation proceeds should be sufficiently high to maintain plume buoyancy and to facilitate simultaneous or subsequent removal of NO_x by selective catalytic reduction with ammonia.

SO_2-absorption processes can be divided into two classes: those using regenerable and those using non-regenerable sorbents. The non-regenerative processes produce a large amount of solid waste for which it is hard to find an application. The regenerable processes facilitate the production of concentrated sulphur compounds. The gas flows obtained upon regeneration of the sorbents may contain SO_2, SO_3, H_2S or even S_n. Regenerative processes using a liquid sorbent exhibit some disadvantages, the most important of which is the low temperature required to provide sufficient absorption capacity. As the absorption is based on physical interaction between the SO_2 molecules and the liquid sorbent (organic solvent), the flue gas has to be cooled to a low temperature (350 K) in order to increase the solubility [1]. After desulphurisation, the flue gas has to be re-heated to minimise corrosion and to avoid plume droop leading to local pollution. Cooling and heating of a large (flue) gas stream causes a considerable loss of energy. Therefore a solid sorbent which captures SO_2 at elevated temperatures (470–870 K) by a chemical interaction seems to be most advantageous. Such sorbents contain a metal oxide capable of forming sulphates or sulphites while in contact with SO_2 and O_2. Flue gas desulphurisation, using a solid sorbent, can be performed in a fluidised bed [2–4], a parallel-passage reactor [5] or a gas–solid trickle-flow reactor [6–8]. These reactors provide an intimate contact between the sorbent and the flue gas at a low pressure drop and are not expected to become ineffective by entrapment of large amounts of dust. Regeneration of the solid sorbent may be brought about by thermal decomposition in air or by chemical regeneration in a reducing environment.

The applicability of a sorbent depends on its absorption rate, its absorption capacity and its case of regeneration. In the past many metal oxides have been screened for their applicability as a regenerable flue-gas desulphurisation sorbent [9,10]. A thermodynamic evaluation by Lowell et al. [9] showed that, in the temperature range 300–1070 K, nearly all metal oxides are capable of sulphate formation by sorption of SO_2 in the presence of O_2. Although with some metal oxides, sulphite formation is also thermodynamically feasible, the sulphites are unstable with respect to sulphate in the presence of oxygen in the flue gas. Thermal regeneration is only feasible for a limited number of metal oxides because of the very high temperatures required for decomposition of the more stable sulphites or sulphates. Measurements by DeBerry and Sladek [10] on the kinetics of SO_2 absorption exhibited by various oxides indicated that CuO and CeO_2 showed the highest absorption rate. The application of these metal oxides has been patented by Shell [11] and Exxon [12], respectively.

Here we report on the absorption and chemical regeneration of two well-characterised copper(oxide)-on-silica sorbents. The reactivity of the sorbents was assessed by measuring the rate of the gas–solid reactions during temperature-programmed absorption, regeneration and oxidation. Special interest was paid to the possible formation of cuprous sulphide (Cu_2S) upon chemical regeneration of a sulphated sorbent, using hydrogen as a reducing agent. Infrared spectroscopy was used to investigate the condition of the surface of the copper (oxide) after various pre-treatments. Along with the experimental results, a brief literature survey on the poisoning of copper by sulphur is presented.

EXPERIMENTAL

The sorbents were prepared by precipitation of copper ions from an aqueous silica suspension. The silica support (Aerosil, Degussa, West Germany) had an initial surface area of 230 m^2 g^{-1}. Deposition of copper on silica by urea decomposition at 363 K brings about reaction of the silica and thus an increase in the total specific surface area, which depends on the metal loading [13]. The copper loading of the sorbent (CuU20) prepared by urea decomposition was 20 wt.% (g Cu/(g Cu + g SiO_2)). Another sorbent was prepared by intentionally precipitating basic copper nitrate, $Cu_2(NO_3)(OH)_3$, having little or no interaction with the silica support, at pH 5.5 and 303 K. This sorbent (CuI20) also had a metal loading of 20 wt.%. The total specific surface area of the sorbents was determined by nitrogen adsorption at 77 K. The copper particle size of the reduced and passivated sorbents was established by transmission electron microscopy. From the copper particle size, a specific copper surface area (m^2 g^{-1} Cu) can be calculated. For comparison purposes, some experiments were done using pure copper powder (Cu p.a., Merck 2703) or the bare silica support.

Activity measurements were performed on powdered samples (particle diameter < 0.3 mm) placed in a microreactor with an internal diameter of 8.0 mm. Approximately 100 mg of sorbent was used. With the pure copper sample, the amount was reduced to 20 mg. In all experiments the flow rate was 50 cm^3 (STP) min^{-1}. The gases were deoxygenated and dehydrated. The composition of the dynamic gas atmospheres is specified in Appendix A.

The activation of the freshly precipitated and dried (air, 390 K) sorbents comprised consecutive calcination, reduction, oxidation, reduction and oxidation treatments (see Appendix A for experimental details). Subsequent exposure of the sorbent to sulfur dioxide at room temperature and linearly increasing the temperature to 770 K yields the temperature-programmed sulphation (TPS) results, dealt with in the next section.

After the TPS experiments, the sorbents were regenerated by a temperature-programmed reduction (TPR) with hydrogen and were subsequently subjected to a temperature-programmed oxidation (TPO). The measurements involved the consumption of hydrogen during TPR, the consumption of oxygen during TPO and the consumption of sulphur dioxide during TPS. The difference in gas composition before and after the reactor was continuously monitored by means of a thermal conductivity detector (TCD).

The CuU20 sorbent was also characterised by infrared transmission–absorption spectroscopy (ITAS). A self-supporting wafer of the sample was made by pressing (1300 kg cm^{-2}, 15 min) the finely powdered sorbent. The wafer was mounted in a gas cell and subjected to thermal treatments up to 770 K in various dynamic gas atmospheres, facilitating a comparison with the temperature-programmed reactions. After each treatment the sorbent was cooled down to room temperature in the absence of adsorbing gas molecules. Subsequently, spectra of the solid sorbent were recorded with a Perkin–Elmer 1720 FT–IR spectrometer. Sixty-four scans were co-added, after which the resultant interferogram was Fourier-transformed to obtain a resolution of 4 cm^{-1} over the spectral range 4000–450 cm^{-1}.

RESULTS AND DISCUSSION

Activation of the sorbents

The deposition of copper ions onto the silica support by means of urea decomposition results in the formation of a sorbent precursor with a high copper dispersion. The structure of the surface compound in this precursor is close to the structure of copper hydrosilicate, the mineral crysocolla [14]. Upon exposure to flue gas at an elevated temperature, chrysocolla does not readily form sulphates. This is probably due to the high (2-dimensional) dispersion of the copper ions over the silica surface and the resulting strong interaction between the copper ions and the silica support [15]. Thus, the sorbent precursor has to be activated by a calcination, reduction, oxidation cycle as described in Appendix A. After preparation, the dried sorbent is calcined in situ to remove both physically and chemically bonded water. Subsequent reduction results in the formation of copper metal particles. During the temperature-programmed reduction, the copper ions are reduced to metal atoms which migrate over the support. As the reduction proceeds the metal atoms agglomerate to form three-dimensional copper particles (clusters). The sorbent precursors used in this work yielded significantly different copper particle sizes. Sorbent CuU20 has the smaller copper particle size of average diameter 3.5–5.0 nm, whereas sorbent CuI20 has a very broad particle size distribution, 5–100 nm. This difference in particle size, as observed by transmission electron microscopy, is due to the intentionally different precipitation conditions. The precursor of sorbent CuU20 exhibits a high dispersion of copper ions over the silica support, whereas the CuI20 precursor contains large $Cu(OH)_3(NO_3)$ crystallites which are not in intimate contact with the support. Reduction of the latter precursor with the poorer dispersion results in the formation of large copper metal particles. Consequently, the size of the final copper particles depends on the initial dispersion of copper ions in the precursor.

Clearly the average copper particle size determines the active surface area of the metal oxide exposed to the gas phase. For instance, with the sorbents used in this work, a copper metal particle size of 5 nm in diameter gives a surface area of ~ 135 m^2 g^{-1} Cu, whereas copper particles of 50 nm in diameter expose only ~ 13.5 m^2 g^{-1} Cu. Furthermore, complete oxidation (and sulphation) of bulk copper becomes very difficult and, hence, slow with increasing thickness of the surface layer of reaction product [16]. For sorbents to have both a high absorption rate and capacity, it is thus necessary to have a small copper particle size. A small copper particle size can only be obtained if the particles exhibit sufficient interaction with the support, both during the precipitation and during any subsequent thermal treatment.

Because the densities of copper oxide (6.4 g cm^{-3}) and copper sulphate (3.6 g cm^{-3}) are lower than the density of copper metal (8.9 g cm^{-3}), the active phase of the sorbent changes in volume upon oxidation/sulphation and reduction/regeneration. If the volume of the completely reduced copper metal particles is normalised to V_{Cu}, the volume of the copper particles in the oxidised state is ~ 1.7 V_{Cu} and the volume occupied by the completely sulphated particles amounts to ~ 6.2 V_{Cu}. The swelling and shrinkage of the copper phase during sulphation and regeneration should not, however, cause sintering of the active material. Therefore, the support should act as a dispersing medium which provides for a high dispersion of the copper particles upon preparation of the sorbent and, furthermore, maintains the initial high dispersion during many absorption–regeneration cycles.

Sulphation and regeneration cycles

Temperature-programmed reduction of the sorbent provides information on the reducibility of the copper phase present and the amount of hydrogen required to reduce the copper species. After calcination, a first reduction of the CuU20 sorbent proceeds at 470 K. Subsequent TPO of the freshly reduced sorbent gave rise to the oxygen uptake shown in Fig. 1a. Oxidation of the highly reactive, reduced copper particles starts at room temperature. Linearly raising the temperature of the sorbent in the oxygen-containing atmosphere causes the oxidation to accelerate at ~ 400 K and ~ 500 K. Full oxidation is reached at 650 K. Reduction of a previously reduced and re-oxidized sorbent starts at 400 K (Fig. 2a). This oxidation–reduction cycle

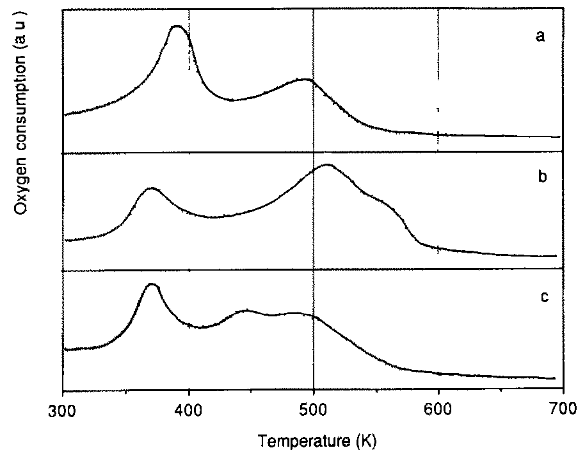

Fig. 1. Temperature-programmed oxidation of CuU20: a, freshly reduced; b, sulphated and regenerated; c, after second regeneration.

was repeated several times without any change in the TPO or TPR profiles. The hydrogen consumption measured by integration of this reduction profile was constant and normalised to 100 a.u. (Table 1).

Temperature-programmed sulphation of a previously oxidised sorbent gives rise to the SO_2-uptake profile shown in Fig. 3a. The sulphation of the sample starts at 570 K. Initially the rate increases with increasing temperatures. After passing through a maximum at 660 K, the reaction rate declines, but the SO_2-consumption never drops to zero, due to the formation of some SO_3 which condenses behind the reactor. In a separate experiment it was established that at temperatures between 670 and 770 K, oxidation of SO_2

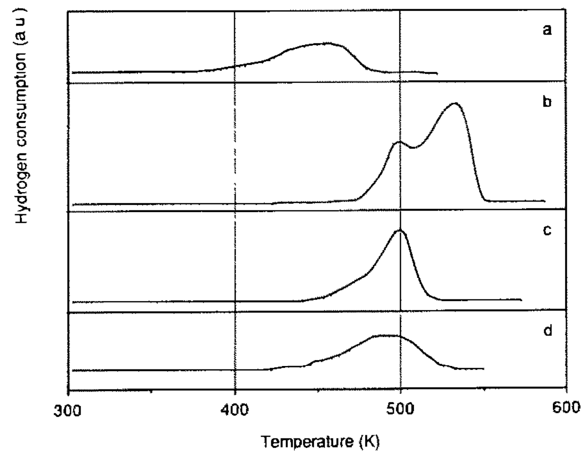

Fig. 2. Temperature-programmed reduction of CuU20: a, freshly activated and oxidised; b, sulphated; c, once regenerated and re-oxidised; d, twice regenerated and re-oxidised.

TABLE 1

Normalised hydrogen consumption (a.u.)

Treatment	CuU20	CuI20
Reduction + oxidation [a]	100	100
Sulphation	293	105
1st regeneration + oxidation	144	110
2nd regeneration + oxidation	122	–
Sulphidation + oxidation	209	196

[a] Independent of the number of oxidation–reduction cycles.

by oxygen to form SO_3 does indeed proceed over a sulphated copper surface, but not over the surface of the silica support. After regeneration and oxidation of the sorbent, sulphation (TPS) proceeds as shown in Fig. 3b. The SO_2-uptake starts at a slightly more elevated temperature and the maximum SO_2-consumption is exhibited at around 680 K, indicating some deactivation of the sorbent. After this small decline of the SO_2-absorption activity upon a first sulphation–regeneration cycle, the CuU20 sorbent shows a stable activity as demonstrated by the many reproductions of the TPS-profile shown in Fig. 3b. Figure 3c shows the rate of SO_2-absorption by a CuU20 sorbent which has not been re-oxidised after regeneration. Thus, at room temperature, the reduced copper particles are exposed to a mixture of oxygen and sulphur dioxide in nitrogen and linearly heated up to 773 K, causing both oxidation and sulphation. It can be seen that a large uptake of sulphur dioxide already occurs at 380 K and complete saturation is observed above 570 K.

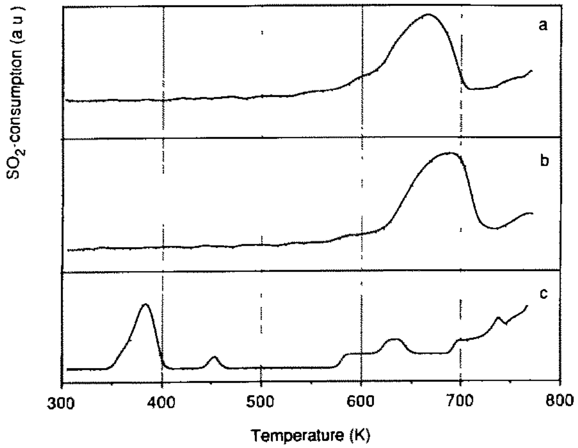

Fig. 3. Temperature-programmed sulphation of CuU20: a, first sulphation; b, second sulphation; c, sulphation without pre-oxidation.

TABLE 2

Equations and thermodynamic data of reactions cited in the text [a]

Reaction	T (K)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})
(1) $CuO + H_2 \rightarrow Cu + H_2O$	300	−100.3	−86.5
	700	−117.5	−93.2
(2) $CuSO_4 + 2H_2 \rightarrow Cu + SO_2 + 2H_2O$	300	−98.2	−11.8
	700	−206.9	−28.0
(3) $2CuSO_4 + 6H_2 \rightarrow Cu_2S + SO_2 + 6H_2O$	300	−433.6	−290.2
	700	−631.2	−175.4
(4) $2H_2S + SO_2 \rightarrow 3/n\ S_n + 2H_2O$	300	−72.9 [b]	−109.9 [b]
	700	−27.8 [b]	−103.0 [b]
(5) $2Cu + SO_2 + 2H_2 \rightarrow Cu_2S + 2H_2O$	300	−244.1	−267.4
	700	−217.8	−259.8
(6) $SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$	300	−191.4	−208.5
	700	−163.7	−218.6
(7) $2CuS + H_2 \rightarrow Cu_2S + H_2S$	300	−21.8	−2.9
	700	−50.1	1.8
(8) $Cu_2S + H_2 \rightarrow 2Cu + H_2S$	300	52.7	58.9
	700	51.2	41.3

[a] Thermodynamic values from Barin and Knacke [31].

[b] For $n = 8$.

Due to its low copper dispersion, sorbent CuI20 shows a poor activity for SO_2-absorption. Thus the TPS-profiles show hardly any SO_2 consumption and the hydrogen consumption (Table 1) is not significantly affected by sulphation–oxidation cycles. The following presentation deals with sorbent CuU20 only.

Regeneration of a completely sulphated sorbent gives rise to the TPR-profile shown in Fig. 2b. The on-set temperature for regeneration (525 K) is significantly higher as compared to the on-set of reduction of the merely oxidised sorbent (Fig. 2a). Furthermore, regeneration of a sulphated sorbent requires an increased amount of hydrogen (Table 1). Both the higher on-set temperature and the increased hydrogen consumption can be explained by the reduction of copper sulphate instead of copper oxide. The presence of copper sulphate in the sulphated sorbent was established by X-ray diffraction (XRD). The increase of hydrogen consumption by a factor of 2.93 cannot, however, be explained if it is assumed that reduction and regeneration proceed according to eqns. (1) and (2), respectively (Table 2). Apparently, regeneration of the sulphated sorbent does not simply proceed according to eqn. (2). It can be argued that the large hydrogen consumption is due to an increased degree of copper reduction and/or the formation of some cuprous sulphide. The reduction of copper sulphate to cuprous sulphide requires a large amount of hydrogen, reaction (3). The formation of some H_2S may even further increase the total hydrogen consumption.

The following experiments were aimed at establishing the origin of the increased hydrogen consumption. In situ XRD during regeneration of the sulphated sorbent shows the formation of metallic copper only. No intermediate solid phase(s) were formed. Thus, it is concluded that, upon regeneration, the bulk of the copper phase is reduced to the metal. Temperature-programmed oxidation of a regenerated CuU20 sorbent, however, shows an altered oxygen uptake as compared to the oxidation of the activated sorbent before sulphation (Fig. 1b). Thus it appears that the interaction between molecular oxygen and the copper phase is modified by the sulphation and regeneration procedures. The increased oxygen consumption around 500 K indicates that the affinity of the copper phase towards oxidation at lower temperatures has decreased. This decrease may either be caused by an increased copper particle size or the presence of some sulphur species (not detectable by XRD) in the copper phase.

The temperature-programmed reduction of the regenerated and subsequently re-oxidised sorbent is shown in Fig. 2c. The on-set temperature for reduction is still higher as compared to reduction of a freshly activated sorbent (Fig. 2a). Furthermore, the hydrogen consumption is again too large, based on eqns. (1) and (2) (Table 1). Subsequent TPO of the sorbent gives rise to the oxidation profile shown in Fig. 1c. The profile shows close resemblance to that of a freshly reduced sorbent (Fig. 1a). Apparently the condition of the sorbent can be changed by an oxidation–reduction cycle, after regeneration of a sulphated sorbent. Subsequent TPR gives rise to the profile shown in Fig. 2d. The on-set temperature and the hydrogen consumption have decreased again (Table 1). Repeating the oxidation–reduction cycle does not further alter the TPO and TPR profiles. In summary, the most distinct difference in the oxidised sorbent before and after sulphation, is reflected in the altered TPR profile (Figs. 2a and 2d) and the increased hydrogen consumption (Table 1).

These results can be explained by assuming the presence of a sulphur species in the regenerated sorbent, which can only be partly removed by a repeated oxidation–reduction cycle.

The formation and nature of the sulphur species present in the regenerated sorbent was investigated in more detail by studying the reactivity of the copper (oxide, sulphide, sulphate) phase towards various dynamic gas atmospheres. During regeneration, both sulphur dioxide and hydrogen are present in the pores of the sorbent. It is thus interesting to study the interaction of sulphur dioxide, as a representative of reactive sulphur oxide species, and hydrogen over a reduced copper surface.

Therefore, a reduced CuU20 sorbent was exposed to a gas atmosphere containing 1% SO_2, and 10% H_2 in N_2, and the hydrogen consumption as a function of the temperature up to 770 K was measured. After 1 h at 770 K, the sorbent was cooled down to room temperature in the same gas atmosphere. The results of this experiment are shown in Fig. 4. At approximately

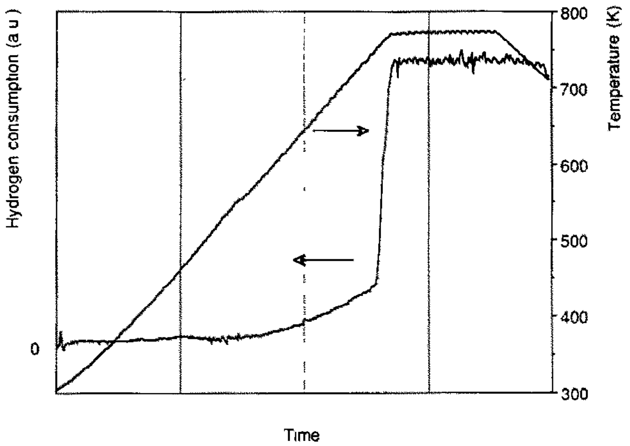

Fig. 4. Hydrogen consumption during temperature-programmed reaction of the sorbent in an atmosphere containing both hydrogen and sulphur dioxide.

670 K, the hydrogen consumption rapidly increases to reach a constant rate at the isotherm temperature of 770 K. As long as the sorbent is kept at 770 K, the hydrogen consumption is constant. At this temperature, formation of hydrogen sulphide (H_2S) was observed. Reaction (4), of H_2S with the SO_2 present in the gas feed, gives rise to the formation of elemental sulphur (S_n), which condenses in the cooler parts downstream from the reactor. Upon cooling the sorbent, the hydrogen consumption drops to zero. At room temperature, the SO_2 and H_2 were flushed from the sorbent with N_2. Subsequent reduction (TPR) of the sorbent shows no hydrogen consumption. XRD characterisation of the sorbent indicates the presence of bulk $Cu_{1.96}S$.

The reactivity of the sorbent was subsequently investigated by TPO. Oxidation of the sorbent requires a more elevated temperature (550 K) as compared to previous results on the reduced/regenerated sorbent (Fig. 5a). Furthermore, the consumption of oxygen was notably increased as compared to the amount of oxygen required to convert the reduced sorbent into an oxidised sorbent. The results of the temperature-programmed reactions and XRD can be explained by the uptake of a considerable amount of sulphur in the reduced copper particles, eqn. (5), and by the reaction of SO_2 and H_2 according to eqn. (6). In conclusion, during regeneration of the sorbent by hydrogen, reaction (6) may occur giving rise to the increased hydrogen consumption shown in Table 1 and the retention of sulphur in the sorbent, lowering its activity and absorption capacity.

After TPO of the sulphided CuU20 sorbent, regeneration gave rise to a hydrogen consumption of 209 a.u., indicating that oxidation of the sorbent did not result in formation of a stoichiometric copper sulphate, as obtained after TPS (Table 1). This may be due to either insufficient sulphur in the sulphided sorbent (Cu_xS, $x > 1$) or to loss of sulphur as SO_2 during

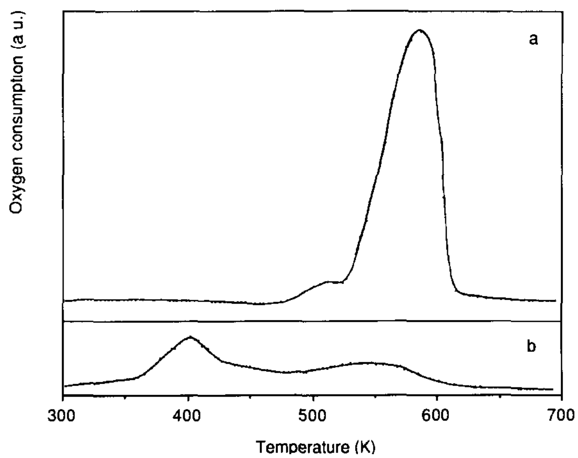

Fig. 5. Temperature-programmed oxidation of CuU20: a, sulphided; b, sulphided, oxidised and regenerated.

oxidation. Temperature-programmed oxidation of the regenerated sorbent gives rise to the oxygen uptake shown in Fig. 5b. This profile is similar to previous results obtained on the reduced/regenerated sorbent. The sorbent with the poor copper dispersion shows that sulphidation of the copper particles, e.g. acceptance of S^{2-} ions, proceeds more easily than conversion into copper sulphate during a TPS experiment (Table 1).

Infrared spectroscopy

The effect of thermal treatments in different gas atmospheres on the formation of Cu–O–S structures was investigated by IR spectroscopy. The spectrum of the freshly activated and reduced sorbent is shown in Fig. 6. The spectrum is typical of silica-supported catalysts and shows major absorption bands in the hydroxyl stretch region (4000–3300 cm^{-1}) and at wavenumbers below 1300 cm^{-1} due to lattice vibrations of the silica support. After oxidation of the sorbent, only small changes in the infrared spectrum were observed. However, after sulphation in an atmosphere containing SO_2, O_2 and N_2, some new absorption bands emerged in the spectrum at 1440, 900 and 700 cm^{-1} (Fig. 6b). Anhydrous bulk copper sulphate shows absorption bands at 1215, 1153, 1085, 962 and 704 cm^{-1} [17]. Unfortunately, as a result of the very low transmittance of the sorbent between 1300 and 940 cm^{-1}, no bands could be detected in this frequency region. The bands present in the spectrum at 900 and 700 cm^{-1} are ascribed to copper sulphate. The wavenumbers of these bands cannot be determined very accurately due to the slope of the background (Fig. 6a). The presence of bulk copper sulphate was also demonstrated by X-ray diffraction. The band at 1440 cm^{-1} cannot, however, be explained by the presence of bulk copper sulphate.

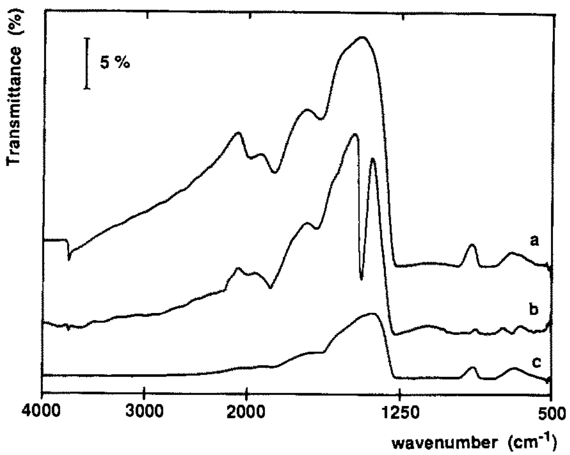

Fig. 6. IR transmission–absorption spectra of CuU20: a, freshly reduced; b, sulphated; c, regenerated.

Reference data of IR absorption bands due to S–O species indicate that organic sulphates and sulphuric acid are the only S–O structures, which exhibit a band in this frequency region. To try to elucidate the origin of the band at 1440 cm^{-1} in the spectrum of the sulphated sorbent, a similar TPS experiment was performed with a wafer of the bare silica support. After sulphation, the spectrum of the silica wafer also showed a band at 1440 cm^{-1}, which could only be removed by purging for 2 h at 723 K in 10% O_2/N_2. With the sorbent, the band was more resistant to evacuation; even after 16 h at 823 K the band had not completely disappeared. A silica wafer which had been saturated with a drop of concentrated sulphuric acid was purged at 573 K to investigate the origin of the band at 1440 cm^{-1}. However, purging at 573 K caused evaporation of the acid and no band at 1440 cm^{-1} was observed. The boiling point of sulphuric acid is 611 K. As no C–H vibrations are observed in the spectrum of the sulphated sorbent, the presence of an organic sulphate seems unlikely. Nor can the band at 1440 cm^{-1} be due to molecular sulphuric acid because of the high purge temperature required to remove the band from the spectrum. In experiments where SO_2 and O_2 were dosed on to the sorbent wafer at room temperature, no 1440 cm^{-1} band was observed. The results indicate that the S–O species is strongly hold on the surface of both silica and the sorbent. This tempts us to suggest that the band is due to a surface sulphate, at the surface of copper sulphate and/or at the silica surface [18].

Upon subsequent regeneration of the sulphated sorbent, the bands at 1440, 900 and 700 cm^{-1} disappear and the transmittance of the wafer is considerable reduced, as compared to the freshly activated sorbent (Fig. 6c). This low transmittance over the full spectral range indicates the presence of either large metal particles (diameter > 15 nm) [19] or the presence of a compound exhibiting a continuous absorption due to unlocalised charge carriers [20]. By repeating the oxidation–reduction cycle, the transmittance is increased. Thus, the low transmittance after regeneration of a sulphated sorbent is not caused by an irreversible increase of the copper particle size but by the presence of a compound showing a mainly continuous absorption over the spectral range. Bulk copper sulphide shows a high absorption over the full spectral range with only one weak band at 960 cm^{-1} [21], thus supporting the conclusions of the TPR/TPO experiments.

Formation of cuprous sulphide

The temperature-programmed reactions indicated an irreversible change in the reactivity of the sorbent with the first sulphation–regeneration cycle. Although the bulk of the copper particles was reduced to the metal as shown by TPR/TPO and XRD, the surface of the particles retained some sulphur, probably as cuprous sulphide, as was demonstrated by ITAS. Therefore, we will discuss the nature of the copper–sulphur bond in some more detail.

The adsorption of sulphur on copper surfaces has been studied by many authors using a variety of analytical techniques [22–30]. It has been established that the copper–sulphur bond of sulphur adsorbed on a copper surface is stronger than the copper–sulphur bonds in bulk copper sulphides. The adsorption of sulphur from H_2S/H_2 mixtures on different metal single-crystal surfaces has been investigated by Benard et al. [22,23]. They have shown a linear relation between the heat of sulphur adsorption and the heat of bulk sulphide formation. Two-dimensional surface sulphides are formed under conditions where bulk sulphide formation does not occur. On the dense single-crystal surfaces, cuprous sulphide is some 10 kJ mol^{-1} more stable than the corresponding bulk sulphide [24]. However, with increasing surface roughness, the heat of sulphur adsorption may increase even further. Especially in supported catalysts containing highly dispersed copper particles with curved surfaces, sulphur may adsorb very strongly at the metal surface. Indeed the adsorption of sulphur in copper-based catalysts is a serious cause of catalyst poisoning [25,26].

Concerning the structure and stoichiometry of the two-dimensional surface sulphide, valuable information is available from investigations on single-crystal surfaces [23,27–30]. For the dense crystal planes of copper, (111), (100), (110) and (210), the saturation sulphur coverages amount to 7.43×10^{14}, 7.24×10^{14}, 6.96×10^{14} and 6.80×10^{14} S atoms/cm^2, respectively [22,28]. These coverages correspond to approximately Cu_2S. The non-ionic character of the copper–sulphur bond makes copper sulphides Cu_xS, very susceptible to formation of non-stoichiometric compounds [26]. This property of the sulphide probably explains the high stability of the two-dimensional surface compound.

During regeneration, the copper sulphate particle is converted into a metallic copper particle covered by a layer of unknown thickness with copper sulphide stoichiometry. The mechanism responsible for the capture of sulphur at the surface of the copper particles is not clear. However, it has been shown that the presence of both SO_2 and H_2 over a copper particle at elevated temperature results in the formation of bulk $Cu_{1.96}S$. Because the amount of SO_2 during regeneration is restricted by the absorption capacity of the sorbent, the concentration of SO_2 during regeneration may be just sufficient to convert only part of the copper particles, namely the surface of the particles. Furthermore, thermodynamics predict the reduction of cupric to cuprous sulphide, (eqn. 7), whereas reduction to copper metal does not occur, eqn. (8). Thus, under reducing conditions, cuprous sulphide is the most stable compound. Cuprous sulphide is even stable against hydrolysis. The sulphide retained in the sorbent after regeneration is converted to sulphate upon oxidation and absorption. The formation of copper sulphide during regeneration lowers both the absorption rate and the capacity, whereas the consumption of reducing agent, per amount of sulphur dioxide removed, is increased. Therefore, the amount of cuprous sulphide formed during regeneration of a sulphated sorbent should be minimised. Careful control over the regeneration conditions (low hydrogen concentration and rapid removal of SO_2 released) may be instrumental in improving the performance of the sorbents.

CONCLUSIONS

Silica-supported copper oxide can be used as a regenerable sorbent for flue gas desulphurisation. The reactivity of such sorbents towards dynamic gas atmospheres containing (mixtures of) nitrogen, hydrogen, oxygen and sulphur dioxide has been investigated by means of temperature-programmed reactions. Additional experiments comprised characterisation of the bulk crystal structure by XRD and characterisation of the surface by infrared transmission–absorption spectroscopy.

A high dispersion of the copper particles is a prerequisite for a high SO_2-absorption rate. After a small initial decrease of the absorption rate, the CuU20 sorbent containing small silica-supported copper particles shows a stable activity, whereas the CuI20 sorbent containing large copper particles shows hardly any activity for SO_2 absorption.

As seen by XRD, sulphation results in the formation of anhydrous bulk copper sulphate. Upon regeneration, the bulk of the copper particles is converted to the metal. From measurements of the total hydrogen consumption during regeneration and subsequent temperature-programmed oxidation, the retention of sulphur, probably as a surface cuprous sulphide, was ascertained. The retention of sulphur in the regenerated sorbent limits the absorption rate and the absorption capacity, whereas the consumption of reducing agent is increased.

It has been shown that the simultaneous presence of hydrogen and sulphur dioxide over a reduced copper surface results in the formation of copper sulphide. This (surface) copper sulphide, present in the sorbent after regeneration, cannot be reduced by hydrogen up to temperatures of 723 K.

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APPENDIX A: EXPERIMENTAL DETAILS OF DIFFERENT TREATMENTS/EXPERIMENTS

Calcination and TPO

Heating the sample in a 2% O_2/He flow from room temperature to 723 K at a temperature gradient of 5 K min^{-1}; then heating isothermally for one hour.

TPR

Heating the sample in a 10% H_2/N_2 flow from room temperature to 723 K at a temperature gradient of 5 K min^{-1}; then heating isothermally for one hour.

TPS

Heating the sample in a 1% SO_2, 4% O_2 and 95% N_2 flow from room temperature to 773 K at a temperature gradient of 5 K min^{-1}; then cooling down after 10 minutes at 773 K.

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