Effect of cobalt (nickel) oxide on the properties of zinc–titanium sorbents for high temperature desulphurization of model coal gas

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Abstract

Zn–Ti–Co(Ni) sorbents for H₂S removal from model hot coal were prepared and characterized. Effects of cobalt (Co) and nickel (Ni) on the sorbents texture, structure, H₂S sorption capacity and regeneration properties were determined. TiO₂ formed mixed metal oxides with CoO and NiO in the fresh sorbents, while TiO₂ and nanocrystalline sulfides of Zn, Co, Ni were found in sulphided ones. The oxidative regeneration of sulphided sorbents re-formed mixed oxides. Sorption capacity of studied materials increased along with an increase of the amount of added Co (Ni) and also with the number of work cycles. Co-doped Zn–Ti materials adsorbed up to 244% more sulfur than these of Zn–Ti, while Ni-doped materials adsorbed ca. twice more H₂S than the corresponding Co-doped sorbents. The addition of Co (Ni) decreased the temperature of ZnS oxidation. The catalytic effect of the Co (Ni) oxides on the oxidation of ZnS was suggested.

Keywords Hot coal gas · Desulphurization · Hydrogen sulphide · Sorbent · Regeneration

Introduction

The present technologies of energy production based on coal combustion, due to environmental reasons and low efficiency, are of low effectiveness. Therefore, the development of better technologies such as supercritical fluidised-bed boilers or technologies based on coal gasification (IGFC, IGCC) is needed. An important problem associated with coal gasification is desulphurization of the obtained coal gas. Currently, the removal of hydrogen sulphide is carried out by wet methods, which requires gas cooling and therefore reduces the efficiency of the entire IGCC installation. The data from a demonstration plant indicated ca. 10% relative increase in the efficiency of the IGCC system as the result of a high temperature desulphurization process application (US Department of Energy 2015). Desulphurization of hot

coal gas has been studied for a number of years; however, a suitable sorbent has still not been developed. Simple and mixed oxides (e.g., of Zn, Fe, Cu, Mn, Ce, Co) are suggested for this purpose (Meng et al. 2010). For improving sorption and regeneration properties as well as number of operating cycles of these materials, addition of V, Co, Ni or Cu oxides is considered (Meng et al. 2010; Atimtay and Harrison 1998; Chomiak and Trawczyński 2015; Pineda et al. 1997).

Zinc based materials show a high reactivity in sulphidation and are easily regenerate in an oxidizing atmosphere. Therefore, they are considered as suitable regenerable sorbents. The disadvantages of zinc sorbents include progressive decay in performance, associated with the lack of stability during sulphidation and incomplete conversion during regeneration. The stability of ZnO at medium temperatures was studied by Bezverkhy et al. (2012). They stated that, during sulphidation at 523–623 K, due to the Kirkendall effect, Zn²⁺ ions diffuse to the grain surface. The metallic zinc accumulated on the surface can evaporate at a high sorption temperature. A ZnO sorbent mixed with a copper oxide (Cu_{0.06}Zn_{0.94}O) was sulphated, and migration of S²⁻ ions inside the sorbent grain was stated. The authors explained this phenomenon by formation of anionic vacancies on the grain surface which accelerate diffusion of sulfur ions inside the grain and improve its sorption capacity. During regeneration, the sulfur migrates from the grain interior

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to its surface; the intensity of this process strongly depends on the temperature and the type of the added metal. Sorption and regeneration properties of zinc-based sorbents are improved by addition of the other components active in H_2S sorption, such as Ni, Co, Cu, Fe, Mn or inerts, e.g.: La_2O_3 , ZrO_2 , bentonite, SiO_2 (Meng et al. 2010; Atimtay and Harrison 1998; Chomiak and Trawczyński 2015; Pineda et al. 1997). Results of theoretical studies of Girard et al. (2014) showed that the concentration of H_2S under equilibrium conditions with NiO is significantly lower than that in the case of CoO. Park et al. (2010) showed that, at medium temperature, the Zn–Ti sorbents doped with Ni are characterised by a higher sorption capacity than those containing of Co.

Complete regeneration of sulphided sorbent is a crucial aspect. Factors affecting the course of regeneration, formation of sulphates and the number of possible work cycles are still not well understood. Ensuring a stable sorption capacity during sulphidation/regeneration cyclic work is another challenge. Park et al. (2010) suggested that the admixture of Ni or Co oxides to Zn-sorbent facilitates regeneration, probably due to a catalytic effect. Girard et al. (2015) studied regeneration of Zn–Mo sorbent and found that the oxidation of MoS_2 apparently lowers the temperature of ZnS oxidation. Despite the development that was made in the studies on sorbents for hot coal gas desulphurization, knowledge of the effect of Co (Ni) addition on the properties of Zn–Ti (ZT) sorbents is still incomplete. To the best of the authors' knowledge, no papers considering the effect of the Co (Ni) component on sorption/regeneration performance of ZT sorbents have been published so far.

The aim of this study was to determine the effect of Co or Ni oxide addition on the desulfurization and regeneration properties of ZT based sorbents. Effects of the cyclic desulphurization/regeneration of Co(Ni) doped ZT sorbent on its texture, morphology, phase composition, capacity of H_2S sorption, as well as on the regenerative properties, are presented and discussed. The composition of the model coal gas used in our study approximately corresponded to that of gas from coal gasification.

Materials and methods

Sorbents preparation

Sorbents were prepared by a slurry concentration method (Zdrazil 2001) using the following raw materials: $Zn(NO_3)_2 \times 6H_2O$ ($\geq 99\%$; Avantor); $Co(NO_3)_2 \times 6H_2O$ ($\geq 99\%$; Acros Organics); $Ni(NO_3)_2 \times 6H_2O$ ($\geq 99\%$; Acros Organics); TiO_2 ($\geq 99\%$; Panareac); natural clay (Družkowska). Example of the synthesis procedure: 15 g of TiO_2 were mixed with 300 cm³ of an aqueous solution of $Zn(NO_3)_2 \times 6H_2O$ and $Co(NO_3)_2 \times 6H_2O$ (37.2 g and

10.92 g respectively; Zn:Co:Ti = 1:0.125:1.5) and stirred for 2 h. Then water was evaporated and the resultant mass was dried in an oven at 423 K for 12 h. Dry material was crushed and calcined under air flow for 6 h at 1173 K. The obtained material was crushed once again, milled for 1 h in a ball mill with a binder (Družkowska clay) at a weight ratio 4:1, and finally calcined at 1173 K for 6 h. Prepared sorbents were denoted as ZT; ZTCo1; ZTCo2; ZTCo3; ZTNi1; ZTNi2 and ZTNi3. The composition of the prepared sorbents (expressed as a ratio of Zn:Co(Ni):Ti) is presented in Table 1.

Apparatus and procedures

Tests of the model coal gas desulphurization, as well as sorbent regeneration, were carried out in a tubular quartz reactor ($d = 8$ mm; $L = 80$ cm) placed in a three-zone tube furnace. 1.5 cm³ of adsorbent particles of 0.4–0.8 mm were loaded into a corundum layer of the reactor. The temperature was controlled below and above the sorbent bed. The sorbent bed was heated (10 K/min) under nitrogen flow up to 873 K, then nitrogen was switched to a model coal gas. Desulphurization was performed using a mixture composed of: H_2 —25 vol.%; CO—49.5 vol.%, CO_2 —20 vol.%; H_2S —0.5 vol.%; CH_4 —5 vol.%. The concentration of H_2S was monitored online (every 15 min) using a gas chromatograph (Perkin-Elmer, Clarus 500) equipped with TCD and FPD detectors. A concentration of 100 ppm H_2S in the gas leaving the reactor was considered as the point of bed breakthrough.

For the calculation of H_2S sorption capacity the following formulas were used:

$$C_S = \frac{m_{Sads.}}{m_{sorb.}} \times 100 = \frac{\left[\frac{P_{H_2S}^{ads.}}{P_{H_2S}^{com.}} \times \sum_0^{t_0} n_{H_2S}^{in} \right] \times M_S}{m_{sorb.}} \times 100$$

$$= \frac{\left[\frac{\int_0^{t_0} (C_{H_2S}^{in} - C_{H_2S}^{out}) dt}{\int_0^{t_0} C_{H_2S}^{in} dt} \times \sum_0^{t_0} n_{H_2S}^{in} \right] \times M_S}{m_{sorb.}} \times 100$$

where C_S is the mass of sulphur adsorbed by 100 g of sorbent [gS/100 g]; $m_{Sads.}$ is the mass of sulphur adsorbed through

Table 1 Sorbents composition

Sorbent	Atomic ratio Zn:Me:Ti
ZT	1:0:1.5
ZTCo1	1:0.125:1.5
ZTCo2	1:0.25:1.5
ZTCo3	1:0.35:1.5
ZTNi1	1:0.125:1.5
ZTNi2	1:0.25:1.5
ZTNi3	1:0.35:1.5

the bed [g]; $m_{sorb.}$ is the sorbent mass [g]; $P_{H_2S}^{ads.}$ is the surface area of the adsorbed hydrogen sulphide [ppmv h]; $P_{H_2S}^{com.}$ is the surface area of introduced hydrogen sulphide [ppmv h]; $\sum_0^{t_0} n_{H_2S}^{in}$ is the amount of hydrogen sulphide introduced into the reactor until the breakthrough of the bed [mol]; $C_{H_2S}^{in}$ is the concentration of hydrogen sulphide fed to the reactor [ppmv]; $C_{H_2S}^{out}$ is the concentration of the hydrogen sulphide leaving the reactor [ppmv]; M_S is the molar mass of sulphur [g/mol].

$$K_{MeO} = \frac{N_{MeS}}{N_{MeO_0}} = \frac{N_{H_2S}^{ads.}}{\sum_0^j N_{Me_jO}} = \frac{\frac{\int_0^{t_0} (C_{H_2S}^{in} - C_{H_2S}^{out}) dt}{\int_0^{t_0} C_{H_2S}^{in} dt} \times \sum_0^{t_0} n_{H_2S}^{in}}{\sum_0^j N_{Me_jO}} \times 100 \quad (2)$$

where K_{MeO} is the active component conversion (oxides to sulphides) [%]; N_{MeS} is the amount of metal sulphides [mol]; N_{MeO_0} is the amount of metal oxides active in the H_2S sorption [mol]; $N_{H_2S}^{ads.}$ is the amount of adsorbed hydrogen sulphide [mol]; $\sum_0^j N_{Me_jO}$ is the sum of the cardinality of active sites in the sorption metal oxides, where j ingredients are active in sorption [mol].

$$W_{H_2S} = \frac{P_{H_2S}^{in} - P_{H_2S}^{out}}{P_{H_2S}^{in}} \times 100 = \frac{\int_0^{t_0} (C_{H_2S}^{in} - C_{H_2S}^{out}) dt}{\int_0^{t_0} C_{H_2S}^{in} dt} \times 100 \quad (3)$$

where W_{H_2S} is the degree of H_2S removal from the gas, until the bed breakthrough (i.e., after t_0) [%].

After reaching the breakthrough point, the bed was flushed with nitrogen and optionally quenched under N_2 flow. Regeneration was carried out using 3 vol.% of O_2 in N_2 (GHSV = 24 000 h^{-1}). The concentration of SO_2 was determined using a Mulator 610 (Maihak) analyser.

The regeneration of spent sorbents was performed according to two different procedures. The first procedure (Procedure I) included a rapid temperature rise from room temperature to 703 K; then the bed was heated up to 923 K (at 2 K/min rate) and held at this temperature. In the second procedure of regeneration (Procedure II), in the first stage, sorbents were regenerated at 703 K (or 793 K, until the rate of SO_2 emission decline was < 5 ppm/min); then the temperature was ramped up to 923 K (2 K/min). Apart from these two procedures, some regeneration tests were performed under isothermal conditions, i.e., sorbent was heated under nitrogen flow up to the fixed temperature and, when it was reached, the nitrogen was replaced with 3 vol.% of O_2 in N_2 .

In multicycle tests, after sulphidation the sorbet was allowed to cool down to ambient temperature and then regeneration according to the indicated procedure was performed. The regenerated sorbent was cooled down to

ambient temperature and then the next cycle of sulphidation/regeneration was started.

Characterisation

The phase composition of the studied materials was determined by X-ray powder diffraction (XRD), using an X'Pert Pro diffractometer (PANalytical Ltd.) with CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$). The average crystallite size of the dominant phase was determined from the broadening of the diffraction lines on the basis of the Scherrer equation (Azároff 1968).

The sample morphology was studied by scanning electron microscopy (Jeol JSM-6610LVnx) with an integrated X-ray energy dispersive spectrometer (EDS) (Oxford Aztec Energy). Due to the low electrical conductivity, samples were sputtered with graphite in a vacuum coater.

The texture of the samples was determined using conventional mercury porosimetry (440 Pascal CE Instruments, pressure 200 MPa), before the test samples were out-gassed at room temperature for 1 h. The pore radius was calculated from the Washburn equation (Washburn 1921).

Results and discussion

Fresh sorbents

Powder XRD analyses of fresh sorbents (Figs. 1, 2) showed the presence of TiO_2 (ZT), Co_2TiO_4 (ZTCO1; ZTCO2; ZTCO3) and $NiZnTiO_4$ (ZTNi1; ZTNi2; ZTNi3). Titania is a main phase occurring in the basic (ZT) sorbent. Addition of CoO into ZT leads to the formation of mixed oxides of which Co_2TiO_4 is dominant, while in the case of Ni doped materials, $NiZnTiO_4$ dominates. The unambiguous assignment of X-ray peaks of Co_2TiO_4 , $ZnCo_2O_4$, Zn_2TiO_4 and

Fig. 1 XRD diffraction patterns of fresh sorbents ZT and ZTCO

Fig. 2 XRD diffraction patterns of fresh sorbents ZT and ZTNi

NiZnTiO₄ is difficult due to the noisiness of the spectrum and partial signal overlapping. This problem is mentioned in numerous reports because it makes it difficult to analyze a phase transformation during cyclic work (Chomiak and Trawczyński 2015; Pineda et al. 1997). There are no signals of Co (Ni) simple oxides in the XRD patterns, probably due to the large excess of TiO₂ used for sorbent preparation. Moreover, the absence of the corresponding diffraction peaks may result from their amorphous or low crystalline state. ZnO signals are present in the diffraction patterns of most of the tested sorbents. The presence of free ZnO in the sorbent is undesirable because it is less resistant to the reduction by hydrogen than the mixed oxides containing this element (Lew et al. 1989, 1992). ZnO, CoO and NiO compete in the formation of mixed oxides with TiO₂. Co (Ni) oxides form mixed oxides with ZnO at lower temperatures compared to TiO₂ which favors formation of these components and prevent phase separation during regeneration (Hull and Trawczyński 2014). The average crystallite size of the dominant phases slightly increases with increasing amounts of added metal (Table 2).

The sorbents studied exhibit low values of the specific surface area (SSA) and total pore volume regardless of the type and amount of components introduced (Table 2), which results from the high temperature of calcination. The SSA

and porosity of ZnTi-based sorbents reported in the literature depend on the synthesis method and generally are not very high. For example, Jung et al. (2005) report for ZnTi-bentonite sorbents SSA = 8.43 m²/g (calcined at 973 K) and 3.24 m²/g (calcined at 1273 K) and pore volumes of 0.26 and 0.31 cm³/g, respectively, while ZT sorbent prepared by coprecipitation and calcined at 973 K showed SSA as high as 18.34 m²/g and pore volume of 0.89 cm³/g. The SSA of the ZTNi sorbents lowers and the average pore size increases with increasing content of Ni, while no relationship is observed in the case of Co-doped sorbents. The latter are characterised by a higher average pore size and higher total volume than in the case of ZTNi.

Desulphurization

Three cycles of sorption/desorption were performed for each sorbent (Table 3, Figs. 3, 4)—regeneration of sulphided sorbents was carried out according to the isothermal procedure at 923 K. The ZT shows the lowest sorption capacity among all studied sorbents—it captured the smallest amount of H₂S during the first (1.6 gS/100 g) and subsequent cycles (1.8 gS/100 g). Addition of Co to ZT leads to materials possessing higher efficiency of H₂S removal. For all sorbents the sorption capacity and the conversion of the active components increases with successive operation cycles. The amounts of the sulfur captured by ZT and ZTCo1 during the first cycle differ only slightly. Doubling the amount of added Co (ZTCo1 vs ZTCo2) results in an almost double increase of captured H₂S. As the Co content increases, the conversion of active components increases, which suggests that the presence of Co promotes the diffusion of sulfide ions into the sorbent grains and consequently the conversion of the active components. A similar effect of CuO on sulfur ion diffusion in ZnO has been reported by Bezverkhly et al. (2012). They observed a rapid increase in the size of ZnS crystallites after doping ZnO with Cu, compared to un-doped material. They explained this phenomenon by a change in the sulphidation mechanism as a result of the introduction of Cu into ZnO. Sulphidation of nanosized ZnO by gaseous H₂S proceeds via the outward growth of ZnS: Zn²⁺ and O²⁻ are transferred to the external surface, where the zinc is combined with sulfur

Table 2 Properties of fresh sorbents doped with Co and Ni

Sorbent	ZT	ZTCo1	ZTCo2	ZTCo3	ZTNi1	ZTNi2	ZTNi3
Total pore volume, cm ³ /g	0.196	0.273	0.296	0.267	0.189	0.223	0.188
Specific surface area, m ² /g	3.5	5.3	7.4	5.7	8.5	4.8	3.8
Average pore diameter, nm	194	175	141	113	87	91	175
Dominant phase	TiO ₂	Co ₂ TiO ₄	Co ₂ TiO ₄	Co ₂ TiO ₄	NiZnTiO ₄	NiZnTiO ₄	NiZnTiO ₄
Average crystallite size, nm	79.3	30.2	54.3	54.7	30.1	31.3	42.7

Table 3 Sorption properties of sorbents: ZT, ZTCo and ZTNi

Sorbent	ZT	ZTCo1	ZTCo2	ZTCo3	ZTNi1	ZTNi2	ZTNi3
First sulfidation cycle							
C_s [gS/100 g]	1.6	1.9	3.3	4.7	6.8	7.4	9.0
K_{MeO} [%]	12.5	12.6	22.0	32.8	38.7	44.2	56.3
Second sulfidation cycle							
C_s [gS/100 g]	1.8	2.4	4.1	5.5	8.0	8.2	11.2
K_{MeO} [%]	14.5	15.5	27.6	38.3	45.5	49.5	70.2
Third sulfidation cycle							
C_s [gS/100 g]	1.8	3.0	4.5	6.2	8.9	9.1	11.4
K_{MeO} [%]	14.5	19.2	30.5	43.2	51.9	54.7	71.4

Fig. 3 Degree of H_2S removal by sorbents: ZT, ZTCo1, ZTCo2 and ZTCo3 **Fig. 4** Degree of H_2S removal by sorbents: ZT, ZTNi1, ZTNi2 and ZTNi3

and oxygen reacts with protons. In the a case of Cu-doped ZnO, sulphidation proceeds by a mechanism of inward growth: S^{2-} diffuses from the external surface to the internal ZnO/ZnS interface, where it exchanges with O^{2-} . This effect is attributed to a significant acceleration of sulfur transport through the Cu-containing ZnS layer due to the presence of sulfur vacancies formed after the charge compensation of Cu^{1+} replacing Zn^{2+} . We suppose that doping of ZT with Co (Ni) can also promote high mobility of sulfur anions in such a sorbent and consequently the conversion of the active components. Jun et al. (2004) also found that the addition of Co (Ni) to ZT increases the conversion rate of ZnO to ZnS. Divergent results are reported regarding the effect of the active component content on the sorption capacity: exponential and linear growth; linear decrease (Wang et al. 2013; Akyurtlu and Akyurtlu 1995; Jun et al. 2004). These discrepancies probably arise from different process conditions and sulfates formation during regeneration (Girard et al. 2014; Wang et al. 2016).

For the ZT and ZTCo sorbents the degree of H_2S removal is higher than 99.2% (Fig. 3); in the case of ZT this parameter decreases with successive work cycles.

Sorption capacity of Ni-containing sorbents significantly exceeds the corresponding values found either for ZTCo or for ZT (Table 3). Additionally, ZTNi sorbents chemisorb H_2S more effectively than basic ZT or ZTCo sorbents. For the ZTCo sorbents, conversion of active components did not exceed 45% in any work cycle, while for ZTNi it was in the range 50–70% (Table 3). This observation is convergent with results presented by Park et al. (2010). The degree of H_2S removal on ZTNi increases in subsequent cycles (Fig. 4).

The XRD patterns (Fig. 5) of sulphided ZTCo sorbents show that TiO_2 is the dominating phase with an average crystallites size almost two times bigger than in the fresh material (Tables 2, 4). During sulphidation zinc present in the mixed metal oxides is converted into dispersed ZnS. X-Ray diffractogram of sulphided ZTCo1 shows no CoS peaks; however, they are seen in the XRD patterns of sulphided ZTCo2 and ZTCo3. Probably the lack of diffraction peaks of CoS results from its high dispersion

Fig. 5 XRD diffraction patterns of sulfided sorbents: ZT, ZTCo1, ZTCo2 and ZTCo3

or low crystallinity (Holder and Schaak 2019). The XRD patterns of all sulphided sorbents show peaks of mixed metal oxides that indicate incomplete conversion of an active metal oxide to sulphided forms (tests were terminated after reaching 100 ppm H_2S in the outlet gas). Park et al. (2010) and Jun et al. (2001) found Co_9S_8 in the sulphided ZTC sorbent; however, their experiments were performed under different conditions.

The X-ray diffraction patterns of the sulphided ZTNi1 and ZTNi2 (Fig. 6) show strong peaks of TiO_2 and intense signals of ZnS are also visible. Signals of Ni_3S_2 are not seen, probably due to low intensity (noisiness) or high dispersion. The presence of zinc oxide and zinc titanate results from incomplete sorbent sulphidation. In the XRD pattern of sulphided ZTNi3, strong peaks of ZnS (average crystallite size 31.6 nm) and less intense signals of TiO_2 and Ni_3S_2 are visible. Jun et al. (2001) reported that NiS in ZTNi sulphided at medium temperature is amorphous whereas Park et al. (2010) found Ni_3S_4 in sulphided NiO/Al_2O_3 with high Ni content (50 wt%). It is considered that the phase composition of the sulphided Ni containing sorbents is determined by the sulphidation

Fig. 6 XRD diffraction patterns of sulfided sorbents: ZT, ZTNi1, ZTNi2 and ZTNi3

parameters: temperature, pressure and H_2S concentration (Wang et al. 2016).

Effect of cyclic operation on the sorbent texture

The properties of sulphided sorbents (after the 4th sulphidation) are presented in Table 4. The total pore volume of ZTCo sorbents lowers after desulphurization tests, irrespective of the Co content, while the SSA increases almost two-fold. This latter effect may be caused by a change of molar volume of the compounds adsorbing the sulfur. The molar volume of ZnS is 1.6 times larger than that of ZnO , while in the case of $ZnSO_4$ it is even 3.1 times larger (Lew et al. 1992). Cyclic changes in molar volume of a material may lead to its fracturing, loss of porosity and development of SSA.

The average pore size of fresh ZTCo(Ni) sorbents increases with the amount of Co(Ni) (Table 2), while after 4 cycles of sulphidation it is significantly lower (Table 4). The SSA and total pore volume of doped sorbents increase after sulphidation—more intensively for these with a higher dopant content.

Table 4 Properties of selected sulfided ZTCo and ZTNi sorbents (in the 4th cycle)

Sorbent	ZT	ZTCo1	ZTCo3	ZTNi1	ZTNi3
Total pore volume, cm^3/g	0.174	0.207	0.219	0.215	0.232
Specific surface area, m^2/g	4.6	9.5	7.8	10.5	13.5
Average pore diameter, nm	176	98	121	77	62
Dominant phase	TiO_2	TiO_2	TiO_2	TiO_2	ZnS
Average crystallite size, nm	87,3	87,0	78,7	93,8	31,6

Table 5 Properties of selected regenerated ZTCo and ZTNi sorbents (at 923 K; after the 3rd work cycle)

Sorbent	ZT	ZTCo1	ZTCo3	ZTNi1	ZTNi3
Total pore volume, cm ³ /g	0.163	0.240	0.258	0.248	0.219
Specific surface area, m ² /g	3.7	10.6	8.0	11.9	10.7
Average pore diameter, nm	193	68	77	73	76
Dominant phase	TiO ₂	Co ₂ TiO ₄	Co ₂ TiO ₄	TiO ₂	TiO ₂
Average crystallite size, nm	77.9	32.6	46.6	49.9	58.1

The SSA and total pore volume of Co (Ni) doped ZT sorbents after 3rd regeneration (three complete cycles of work) are higher compared to the corresponding values of fresh sorbents (Table 5) and are close to the corresponding values determined for sulfided materials.

The effect of sulphidation/regeneration cycles on the texture of the ZT sorbents is still ambiguous. Jung et al. (2005) reported results similar to ours: an increase of SSA of the ZT sorbent calcined at 923 K after 2 and 10 cycles of operation, while total porosity increased after 2 cycles and decreased significantly after 10 cycles. In the case of the sorbent calcined at 1273 K, the SSA increased after 2 cycles of operation and decreased significantly after 10 cycles, while the total porosity decreased in both cases. On the other hand, Huang et al. (2008) report that sulphided ZT sorbent exhibit lower SSA and total pore volume due to ZnS formation (large molecular volume) while regenerated sorbent shows larger pore volume and SSA than fresh material.

The content of sulphates(VI) in the regenerated sorbents after 4 cycles of work was determined. It was found, that the fresh sorbents contain a small amount of SO₄²⁻ (ca. 0.2 mg SO₄²⁻/g), probably introduced with the binder. After 4 cycles of work (isothermal regeneration at 873 K), the

sulphates(VI) contents were 3.8; 1.8 and 4.8 mg SO₄²⁻/g respectively in ZT, ZTNi3 and in ZTCo3.

Comparison of representative images of the surface of fresh and regenerated sorbents shows that repeated cycles of sulphidation/regeneration do not change their morphology significantly (Figs. 7, 8, 9). On the surface of the fresh ZT, large granules are observed; similar granules are visible on its surface after three cycles of regeneration, however they seem to be sintered. A similar conclusion can be drawn by comparing images of the surface of fresh and regenerated sorbents containing Co (Ni): the surface of regenerated materials seems to be more solid and composed of build with finer grains.

Regeneration

During sulphidation, zinc embedded in the mixed metal oxides forms nanocrystalline ZnS. Girard et al. (2014) reported that pure ZnS oxidizes (maximum of SO₂ concentration in tail gas) at temperatures > 873 K. In the case of ZT regeneration (procedure I), oxidation of ZnS begins at a temperature of ca. 703 K (Fig. 10)—the concentration of SO₂ in tail gas increases with temperature and already at

Fig. 7 SEM images of fresh (A) and regenerated (B) ZT sorbent

Fig. 8 SEM images of fresh (A) and regenerated (B) ZTCO₃ sorbent

Fig. 9 SEM images of fresh (A) and regenerated (B) ZTNi₃ sorbent

Fig. 10 SO₂ breakthrough curves during regeneration for sorbent ZT. First procedure of regeneration

Fig. 11 The SO₂ emission spectrum from the sorbent ZT. Effect of the regeneration temperature (isothermal)

Fig. 12 Effect of Co content on SO₂ emission during ZTCo regeneration. First procedure of regeneration

$T > 823$ K, under isothermal conditions (Fig. 11), oxidation takes places quite effectively.

The addition of Co into ZT does not significantly affect the initial temperature of reaction with oxygen during regeneration of the corresponding sorbent, but changes the concentration profile of SO₂ in the tail gas (Fig. 12). Oxidation of sulphided ZTCo starts at ca. 693 K, thus at a temperature similar to that determined for ZT. However unlike ZT, the concentration of SO₂ in tail gas increases much faster with temperature and the Co sorbent contains more when it is higher. In the case of ZTCo1 (the lowest Co content), SO₂ concentration stabilizes in ca. 30 min up to temperature of ca. 773 K and then rapidly increases (for the ZT sorbent a surge in SO₂ concentration was observed at ca. 823 K). For ZTCo2, already at ca. 693 K the concentration of SO₂ is out of the analyser measuring range (3500 ppm), then decreases for a short period (until the temperature reaches 773 K) and again significantly increases. In the case of ZTCo3, the concentration of SO₂ throughout the whole regeneration period (up to the 923 K) remains out of the measuring range.

Higher reactivity of Co sulfide relative to ZnS with oxygen makes regeneration last for a similar period of time as in the case of ZT, even though the former captured more sulfur (Table 3).

Tests of regeneration according to Procedure II (Fig. 13) were aimed to explain the effect of CoS oxidation on the apparent decrease of the ZnS regeneration temperature (whether there exists, e.g., bed overheating). During the first stage of ZTCo regeneration according to Procedure II, the SO₂ emission increases with Co content. During the second step of regeneration the intensity of SO₂ emissions increases with temperature. After the first step of regeneration (isothermally at 703 K) ZTCo3 does not contain CoS, as was proven by XRD analysis (Fig. 16). Because the CoS was oxidized at lower temperature, one can therefore assume that emission of SO₂ during the second step of regeneration is a

Fig. 13 SO₂ breakthrough curves for ZTCo sorbents. Second procedure of regeneration

result of ZnS oxidation. For all ZTCo sorbents regenerated according to Procedure II, emission of SO₂ occurs intensely at ca. 793 K (for ZT a maximum of SO₂ emission occurs at ca. 873 K; Fig. 10) and this effect does not depend on the amount of incorporated Co. Addition of Co to ZT sorbent lowers the temperature of ZnS oxidation. Regeneration at low temperature (703 K) results in CoS oxidation. One can suppose that oxidation of ZnS in ZTCo occurs at lower temperatures than in the case of ZnS in ZT, due to the catalytic effect of the Co and not due to the bed overheating.

Regardless of Ni content, the oxidation of sulphided ZTNi sorbents (Procedure I) starts at ca. 708 K (Fig. 14) and intense emission of SO₂ occurs already at 723 K. Decrease of SO₂ concentration occurs after ca. 120 min of regeneration, independent of the amount of Ni. The profiles of SO₂ concentration in tail gas are very similar for all these sorbents.

Regeneration of ZTNi according to Procedure II (Fig. 15) showed that the regeneration at 703 K is not effective the

Fig. 14 Effect of Ni content on SO₂ emission during ZTNi regeneration. First procedure of regeneration

Fig. 15 SO₂ breakthrough curves for ZTNi sorbents. Second procedure of regeneration

Fig. 16 XRD patterns of regenerated sorbents: ZT, ZTCO1 and ZTCO3

Fig. 17 XRD patterns of regenerated sorbents ZT and ZTNi1

Fig. 18 XRD patterns of regenerated sorbents ZT and ZTNi3

maximum of SO₂ concentration was ca. 2700 ppm and, even after 370 min, the concentration of SO₂ was higher than 900 ppm. Furthermore, sorbent regenerated at this temperature still contains NiS_{1.03} (Fig. 17). These observations indicate a significant difference between sorbents doped with Co and Ni, respectively. 703 K is a sufficient temperature to oxidize CoS, while regeneration of Ni-containing sorbent requires higher temperature. Therefore, the temperature of regeneration was raised up to 793 K (Fig. 15). At this temperature, at the initial stage of regeneration, the SO₂ emission from ZTNi2 (and ZTNi3) is higher than 3500 ppm and then under isothermal conditions, quickly lowers with time.

If the first stage of regeneration (Procedure II) was carried out at 703 K, the concentration of SO₂ in tail gas during the second stage of regeneration (higher temperatures) was very high and for ZTNi1 emission continued during ca. 400 min. When the first stage of ZTNi2 and ZTNi3 regeneration was performed at 793 K, the concentration of SO₂ during the second stage of regeneration was low, despite higher (than for ZTNi1) “sulfur” load on both sorbents. For both temperature modes (703 K and 793 K), just like in the case of ZTCO sorbents, in the second regeneration stage the temperature at which the oxidation of ZnS occurs intensely (> 3500 ppm SO₂), is lowered by Ni addition. A small emission of SO₂ at 793 – 923 K observed for ZTNi2 and ZTNi3 (Fig. 15) suggests that ZnS oxidation in both sorbents (contrary to ZT (Fig. 11)) already occurs at 793 K. One can state that Ni oxide lowers the temperature (catalytic effect) of ZnS oxidation in sulphided ZTNi in comparison to ZT.

The XRD patterns of ZTCO1 and ZTCO3 partially regenerated at 703 K show strong peaks of ZnS and weaker ones of Zn₂Ti₃O₈. There are no peaks of CoS (Fig. 16b, d) and of Co oxides—the latter probably are highly dispersed. The presence of mixed oxide Zn₂Ti₃O₈ indicates an incomplete

conversion of this active component during the sulphidation step or it was re-formed during long-term regeneration.

In the X-ray diffractograms of ZTNi sorbents regenerated at 703 K (Figs. 17b, 18b), peaks of TiO_2 , $\text{NiS}_{1.03}$ and ZnS (dominant) are present. It means that regeneration at 703 K is insufficient for effective oxidation of Ni sulfide and results in only poor SO_2 emission (Fig. 15). The ZTNi sorbents regenerated at 793 K contain ZnS (low intensity peaks), TiO_2 , ZnO; and NiZnTiO_4 . After regeneration at 923 K there is no ZnS (Figs. 17d, 18d), while there are peaks arising from ZnO and NiZnTiO_4 , and peaks assigned to TiO_2 are also observed.

Summarizing the above results for sorbents regeneration, one can state that the addition of Co (Ni) oxides to ZT sorbent lowers the temperature of ZnS oxidation. This effect can be explained by the catalytic action of these oxides—they are known as oxidation catalysts—as well as by overheating of sorbent bed by heat produced during the oxidation of Co(Ni) sulfides (Heyes et al. 1982; Deng and Tüysüz 2014; Xie et al. 2010). Girard et al. (2015) reported that heat produced by oxidation of MoS_2 (in ZnMo sorbents) overheats the sorbent bed and seemingly decreases the ZnS regeneration temperature. The lack of correlation between the amount of added Co(Ni) and the temperature at which sorbent oxidation begins (increase in heat release) suggests that Co(Ni) oxides catalyse ZnS oxidation. Regeneration according to Procedure I favours bed overheating, while under the conditions used in the Procedure II most of the Co (Ni) sulfides are oxidised at low temperatures. The temperature of intense regeneration of ZnS (high concentration of SO_2 in the tail gas) in ZTCo(Ni) is still lower than in the case of ZT. The catalytic effect of Co/Ni compounds on the temperature of regeneration is also suggested by Park et al. (2010) and Jun et al. (2001).

Conclusions

The addition of Co or Ni oxides to the Zn–Ti sorbent improves its desulphurization properties and lowers the temperature of its regeneration as well. Oxides of Co(Ni) incorporated into Zn–Ti sorbent form mixed metal oxides with a spinel-like structure and significantly improve H_2S sorption capacity, the degree of H_2S removal and the conversion of active components until the bed breakthrough. Sorption capacity of ZTCo(Ni) increases with the amount of incorporated Co (Ni). Addition of Ni leads to sorbents possessing higher sorption capacity than those of Co doped ones. Sulphidation of Co (Ni) doped Zn–Ti sorbents results in decomposition of mixed metal oxides and formation of the corresponding metal sulfides and TiO_2 . The metal sulfides are highly dispersed in the whole volume of sorbent grains.

The addition of Co (Ni) oxides to Zn–Ti sorbent affects also the course of regeneration of sulphided sorbent. Sulfides of Co (Ni) are oxidized at a lower temperature than ZnS. Oxides of Co (Ni) formed during oxidation of sulphided sorbent catalyze the oxidation of ZnS, so that it occurs at a lower temperature than in the case of undoped Zn–Ti sorbent. Finally, mixed metal oxides containing CoO or NiO are formed again as a result of regeneration at 923 K.

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Declarations

Conflict of interest The authors declare that the research is in compliance with ethical standards, and they have no conflict of interest.

Human and animal rights This article does not contain any studies with human participants or animals performed by any of the authors.

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