

COMPARISON OF CaO, ZnO AND Fe₂O₃ AS H₂S ADSORBENTS
AT HIGH TEMPERATURES

by

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ABSTRACT

CaO, ZnO and Fe₂O₃ oxides were compared as solid adsorbents for H₂S removal from hot gas. Increasing the temperature from 600° to 800°C increased the H₂S removal in the presence of CaO but decreased it in the presence of Fe₂O₃. For ZnO, the temperature change had little effect on its adsorption. The bulk adsorption capacity was the largest for Fe₂O₃ followed by CaO and ZnO. When the results were normalized to a unit of surface area, the adsorption capacity for ZnO was the largest followed by Fe₂O₃ and CaO.

The adsorption of H₂S was accompanied by its decomposition. In the early stages, decomposition was the most extensive in the presence of CaO. With time on stream the difference in H₂S decomposition, measured by H₂ yields, became smaller.

INTRODUCTION

Purification is an essential step prior to utilization of combustible gases. In this respect the particulate matter and corrosive components must be removed to avoid detrimental effects on material and the environment. Among the latter, a great deal of attention has been directed to sulphur-containing species, where H_2S is usually the most abundant and the most stable compound.

The formation of H_2S accompanies many industrial processes, e.g., pyrolysis, cracking, hydrocracking, hydrorefining, in which H_2S is usually in the mixture with H_2 , CH_4 and higher hydrocarbons. After H_2S removal these gases could be used as valuable fuels or as a source of petrochemicals. On a commercial scale H_2S is removed by wet scrubbing techniques. This step results in a loss of H_2 bound in H_2S . It would be a significant achievement if H_2S could be decomposed in order to reuse the H_2 . Inevitably, such a route would require a solid catalyst and temperatures higher than those applied in wet purifications processes.

Another group of gases containing H_2S are those from gasification. Under reducing conditions, such as those usually applied during moving bed and fluidized bed gasification a substantial portion of S present in the feedstock is converted to H_2S . The H_2S removal is essential prior to utilization of gasification products either as fuel gas or as synthesis gas. In the former, the use in combined cycle power generation has been thoroughly investigated. The present status of this route indicates that the purification at a near gasification temperature is required to make this route economically viable.

Attempts to commercialize the combined cycle prompted the search for solid adsorbents which can efficiently and economically remove S-containing species. Most of the effort has been devoted to materials containing Zn, Co, and Fe. Among those CaO , ZnO and Fe_2O_3 have been frequently tested. However, a study comparing the performance of these oxides on a similar basis has not yet been published. The approach used in the present study involves a normalization of the H_2S adsorption to a unit of surface area of the oxides.

EXPERIMENTAL

Materials

The CaO and ZnO oxides were certified Fisher products and Fe_2O_3 was a reagent product of J.T. Baker Co. The powders of these oxides were pelletized using 2% binder (stearic acid) to produce pellets of 1.5 mm in diameter and 1.5 mm high. To remove the binder the pellets were roasted at 500°C overnight.

The mixture of $\text{N}_2+\text{H}_2\text{S}$ (10 vol % of H_2S) was of the UHP grade and was supplied by the Liquid Air Co.

Apparatus and Procedure

The experimental system consisted of a vertical reactor made of Vycor glass (10 mm ID). The pellets were supported in the middle of the reactor by a quartz wool. For each experiment about 2 g of accurately weighed adsorbent were used. The reactor was externally heated by a Lindberg furnace. The gas mixture entered the reactor at the bottom.

The flow of gases was monitored by a Brookes flowmeter. The gas exiting the reactor passed a Bolston filter before entering the analysis system.

Prior to the experimental run the reactor, loaded with pellets was heated in the stream of N_2 . After the experimental temperature was reached and stabilized the N_2 was replaced by a mixture of N_2 and H_2S . From that point the changes in the composition of exiting gas were followed. The flow rate of the gas mixture was maintained at 0.1 L/min.

Analytical Procedure

A multicomponent on line mass spectrometer was used to analyse the exiting gas. This involved the determination of H_2S , H_2 and SO_2 in the mixture with N_2 . A data system attached to the mass spectroscopie provided composition printouts every 2 min.

The arrangement of the mass spectroscopie allowed the determination of H_2S in concentrations lower than 2.5 vol %. The amount of H_2S in excess of 2.5% was estimated from the peak of mass 32 which was the second most abundant peak from fragmentation of H_2S . It was established from the calibration curve that this peak was a 0.4 fraction of the parent peak which was the most abundant. The detection limit of the system was 0.01 vol % of H_2S .

RESULTS AND DISCUSSION

Adsorption Capacity of the Oxides

The concentration-time profiles for the reaction of H_2S with CaO , ZnO and Fe_2O_3 were obtained at 600° , 700° and $800^\circ C$ in the presence of about 2 g of adsorbent using the $N_2 + H_2S$ mixture containing 10% H_2S . The pattern in reactions of H_2S with the oxides may be obtained when the sum of $H_2 + H_2S$ concentrations in exiting gas is subtracted from 10. At the same time the change in H_2 concentration reflected the pattern in H_2S decomposition. These trends at $700^\circ C$ are shown in Fig. 1. These profiles were used to estimate the break points, i.e., the time at which the H_2S concentration in exiting gas reached 1000 ppm (Table 1). This point was chosen arbitrarily to make a comparison of the adsorbent performance. The data suggests that ZnO is the least whereas Fe_2O_3 the most efficient except at temperature of $800^\circ C$ when CaO appears to be the best.

The results shown in Table 1 indicate the effect of temperature on the reaction of H_2S with the oxides. Thus, in case of CaO the gradual increase of temperature from 600° to $800^\circ C$ resulted in an increase of the break point time indicating an improved performance of CaO at higher temperatures. For ZnO little change in the break point time was observed. On the other hand in case of Fe_2O_3 the time at which the H_2S concentration in exiting gas reached 1000 ppm decreased with increasing temperature.

In addition to H_2S and H_2 the concentrations of SO_2 were also followed. For CaO and ZnO the SO_2 was present in the exiting gas in trace quantities only. In the presence of Fe_2O_3 , relatively large quantities of SO_2 were formed in the initial stages of adsorption. Thus, after about 10 min of adsorption at 600° and $800^\circ C$ the SO_2 concentration in the exiting gas was 0.7% and 1.2%, respectively. At break times shown in Table 1 at 600° and $800^\circ C$ the concentration of SO_2 in the exiting gas was about 2500 ppm and 6000 ppm, respectively. It is believed that the SO_2 formation is associated with the conversion of Fe_2O_3 to FeO .

It is assumed that at the point where the sum of H_2 and H_2S is equal to 10 no further sulphur uptake via the exchange of oxygen ions by sulphur ions takes place. These times, together with concentration of H_2 in the exiting gas in the saturation region are summarized in Table 1. In all cases the H_2 concentration was higher than that from the blank run (e.g., at $700^\circ C$ the

H_2 concentration was about 0.2%) suggesting some catalytic effects of the sulphided solids on H_2S decomposition.

The trends in H_2 formation for each oxide were different. In the initial stages the H_2 yields were largest for CaO followed by ZnO. For Fe_2O_3 , even at $800^\circ C$, the H_2 yield was much lower than that observed in the blank run. After about 50 min the H_2 concentration in the presence of Fe_2O_3 began to increase, presumably due to the catalytic effects of FeS (Nishizawa et al, 1979). It appears that the main differences in trends of H_2 formation can be traced to the first 10 min of adsorption. For example, for CaO the steep increase in H_2 concentration occurs earlier than that of H_2S concentration, whereas for ZnO the H_2 appearance coincides with the steep increase of H_2S concentration. This suggests that CaO may catalyze the H_2S decomposition. As soon as the sulphidation of CaO reached a certain level the rate of H_2 formation attained a steady state. Low H_2 yields in the early stages in the presence of ZnO suggest that H_2S reacts preferentially via anion exchange leading to ZnS and H_2O .

The curves shown in Fig. 1 are suitable for estimating the amount of H_2S being either adsorbed or decomposed in the presence of corresponding oxides. The calculation of the results shown in Fig. 2 was based on the Simpson's method. The temperature increase from 600° to $800^\circ C$ had little effect on the H_2S adsorption by ZnO and Fe_2O_3 , whereas in the presence of CaO the adsorption increased. According to these results the Fe_2O_3 had the highest adsorption capacity per gram of oxide followed by CaO and ZnO. The estimated adsorption capacities are in agreement with the S content of the adsorbents determined at the end of experiments (Table 2).

As the results in Fig. 2 show the relative trends in H_2S decomposition differed from those of H_2S adsorption. The decomposition was fastest in the presence of CaO followed by ZnO and Fe_2O_3 . In the presence of CaO and ZnO the decomposition increased with increasing temperature.

Using the stepwise integration of the curves such as shown in Fig. 1 cumulative amounts of H_2S either adsorbed or decomposed could be obtained. The results of these calculations for the experiments performed at 600° and $800^\circ C$ are shown in Fig. 3. These correlations indicate the difference in the rate of reactions, which for Fe_2O_3 appears to be the highest. For CaO and ZnO the rate of adsorption began to decrease at early stages.

Relative rates of adsorption changed drastically when the data in Fig. 3 were normalized to the unit of surface area (Fig. 4). For these calculations the initial surface area of oxides was used (e.g., CaO 12.8 m²/g, ZnO 3.0 m²/g and Fe₂O₃ 10.4 m²/g by N₂ BET). Thus, in the whole time interval, the ZnO exhibited a markedly higher rate of adsorption than CaO. The data further suggest that the state of Fe₂O₃ saturation by S is reached faster than that of ZnO and CaO. This difference may be attributed partly to the difference between surface structures attained during the adsorption. Therefore, the replacement of O by S for relatively small Ca cations at the surface of crystal may effectively block unconverted sites thus making them unavailable for reactions. Because of the larger size of Fe cations, such effects in the presence of Fe₂O₃ should be less pronounced. In the case of ZnO the time of saturation is affected by a relatively small surface area. Here, the diffusion limitations caused by the product layer on the outer parts of particles will be the most pronounced, compared with CaO and Fe₂O₃.

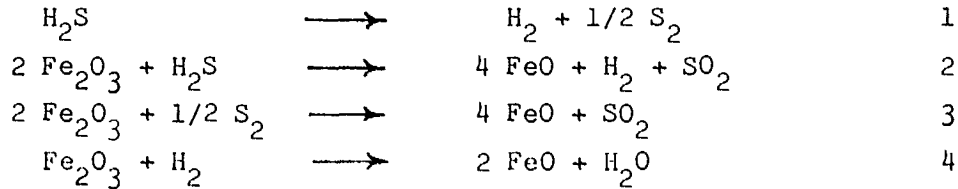
Mechanism of H₂S Action with the Oxides

For all three oxides only trace quantities of H₂S were present in exiting gas in the early stages of adsorption. This confirms extensive reactions of H₂S with the oxides. Besides the H₂S adsorption some other reactions occurred as well. This is indicated by the presence of H₂ and SO₂ in the exiting gas.

For CaO a rapid H₂ build up was observed in very early stages of adsorption. This was accompanied by the accumulation of elemental sulphur on cold parts of the reactor. The H₂ build up leveled off at about break point time. Then, at least two different reactions of CaO with H₂S take place, i.e., one in which H₂S is being decomposed and the other in which H₂S is being consumed presumably via the reaction in which O ions are being replaced by S ions. Some other minor reactions may also occur as indicated by the presence of trace quantities of SO₂ in the exiting gas.

In case of ZnO the conversion to ZnS is believed to be the main reaction taking place during the early stages of adsorption. The H₂ concentration increase in the exiting gas, over that observed during the blank run, was noticed only after certain level of sulphidation has been reached. This suggests that the ZnS may have some catalytic effects on H₂S decomposition.

The presence of relatively large quantities of SO_2 in exiting gas in the early stages, suggests that the mechanism of H_2S action with Fe_2O_3 is more complex. To explain the origin of SO_2 the following set of reactions is proposed:



According to this mechanism the SO_2 was formed via oxidation of H_2S and of elemental sulphur by Fe_2O_3 . The positive log K values for the reactions 2 and 3 at 1000°K (Barin and Knacke, 1973) are in support of this mechanism. The consumption of H_2 via the reaction 4 is thermodynamically favorable as well. This may then explain the absence of H_2 in exiting gas in the early stages of adsorption.

A highly unfavorable thermodynamics for the oxidation of H_2S and of elemental sulphur by CaO and ZnO as well as for their reduction by H_2 represent a major difference in comparison with Fe_2O_3 . It is believed that also in case of Fe_2O_3 it is the FeO species which is effectively trapping H_2S at high temperatures via the exchange of O ions, similarly as in the case of CaO and ZnO .

CONCLUSIONS

Based on the time at which the concentration of H_2S in the exiting gas reached 1000 ppm the temperature increase from 600° to 800°C increased the H_2S removal from hot gas in the presence of CaO but decreased it in the presence of Fe_2O_2 . In case of ZnO the temperature change had little effect. The amount of H_2S adsorbed per gram of oxide, calculated from the area under curves as shown in Fig. 1, increased in the presence of CaO but exhibited little change in the presence of ZnO and Fe_2O_3 with the temperature increase. Also the amount of H_2S decomposed, calculated in similar manner as that of H_2S adsorbed, increased for CaO and ZnO but changed little for Fe_2O_3 .

Among the oxides, Fe_2O_3 had the largest capacity for sulphur per gram followed by CaO and ZnO . However, this order changed when the capacity was expressed per unit of surface area, i.e., the largest capacity had ZnO fol-

lowed by Fe_2O_3 and CaO . This proves that the surface structure of oxides is the essential parameter influencing their adsorption capacities.

The mechanism of intimate action of H_2S differed from oxide to oxide. For CaO , the presence of H_2 in exiting gas confirmed the H_2S decomposition during the rapid H_2S adsorption. In the presence of ZnO and Fe_2O_3 the H_2 appearance coincided with a rapid build up of H_2S in the exiting gas. Relatively large concentrations of SO_2 in the exiting gas in the presence of Fe_2O_3 during the early stages were attributed to the oxidation of elemental sulphur and of H_2S by the oxide. Such reaction is thermodynamically unfavorable for ZnO and Fe_2O_3 .

REFERENCES

1. Barin, I., and Knacke, O. "Thermochemical properties of inorganic substances", Springer-Verlag, 1973.
2. Nishizawa, T., Tanaka, H., and Hirota, K., Int. Chem. Eng., 1979, 19, 3, 517.

Table 1 - Break point time, saturation time and hydrogen concentration
in exiting gas at this time

Oxide	Temperature	Break point time ¹	Saturation time ²	H ₂ concentration
	°C	min	min	vol %
CaO	600	4	170	0.7
	700	8	140	1.1
	800	17	140	1.9
ZnO	600	4	150	0.5
	700	5	130	1.0
	800	5	140	2.0
Fe ₂ O ₃	600	32	100	0.7
	700	20	110	1.2
	800	15	150	1.7

¹ time at which the concentration of H₂S in exiting gas reached 1000 ppm

² time at which the sum of H₂ + H₂S in exiting gas reached 10

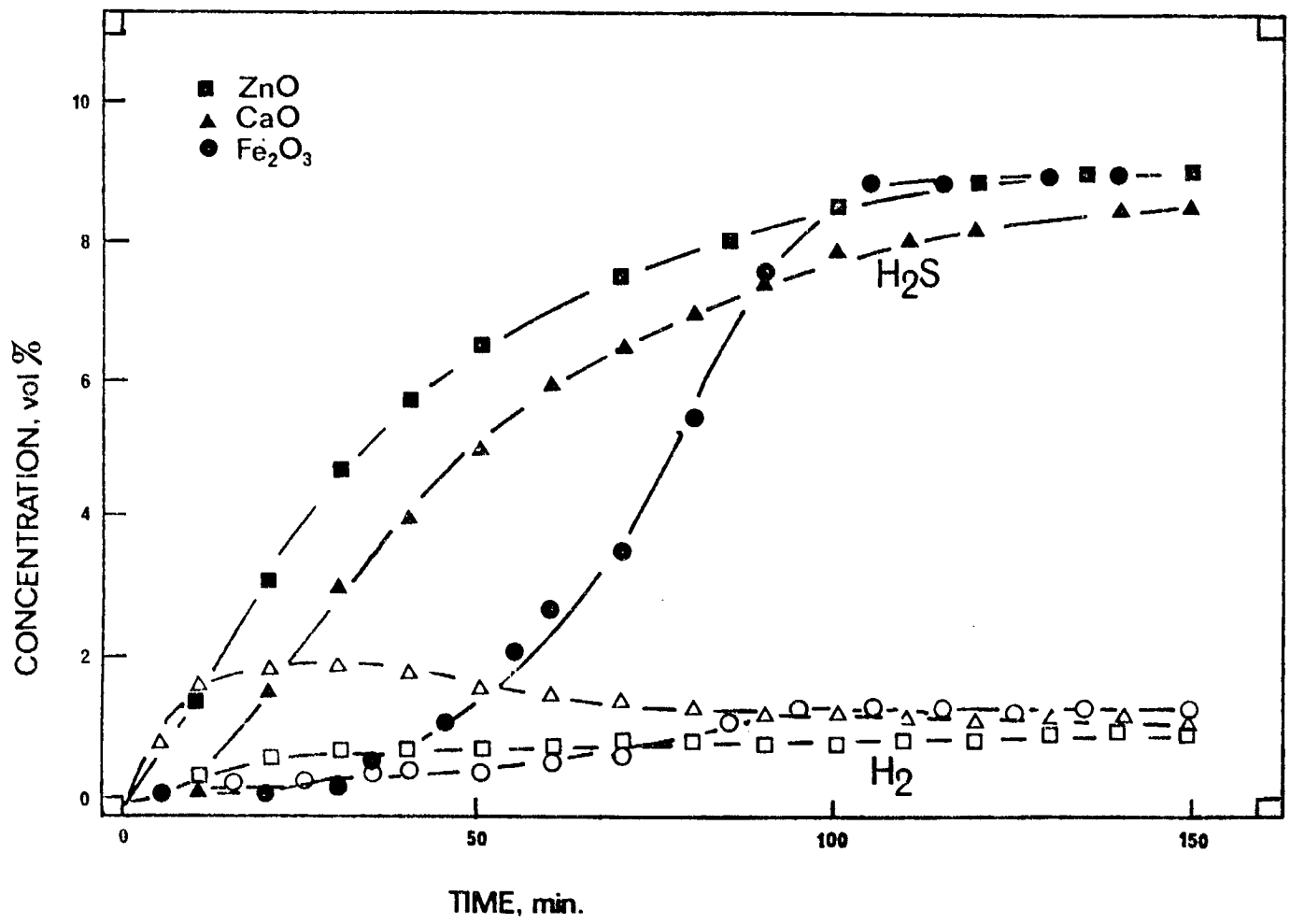
Table 2 - Content of sulphur in adsorbents at the
end of experiments

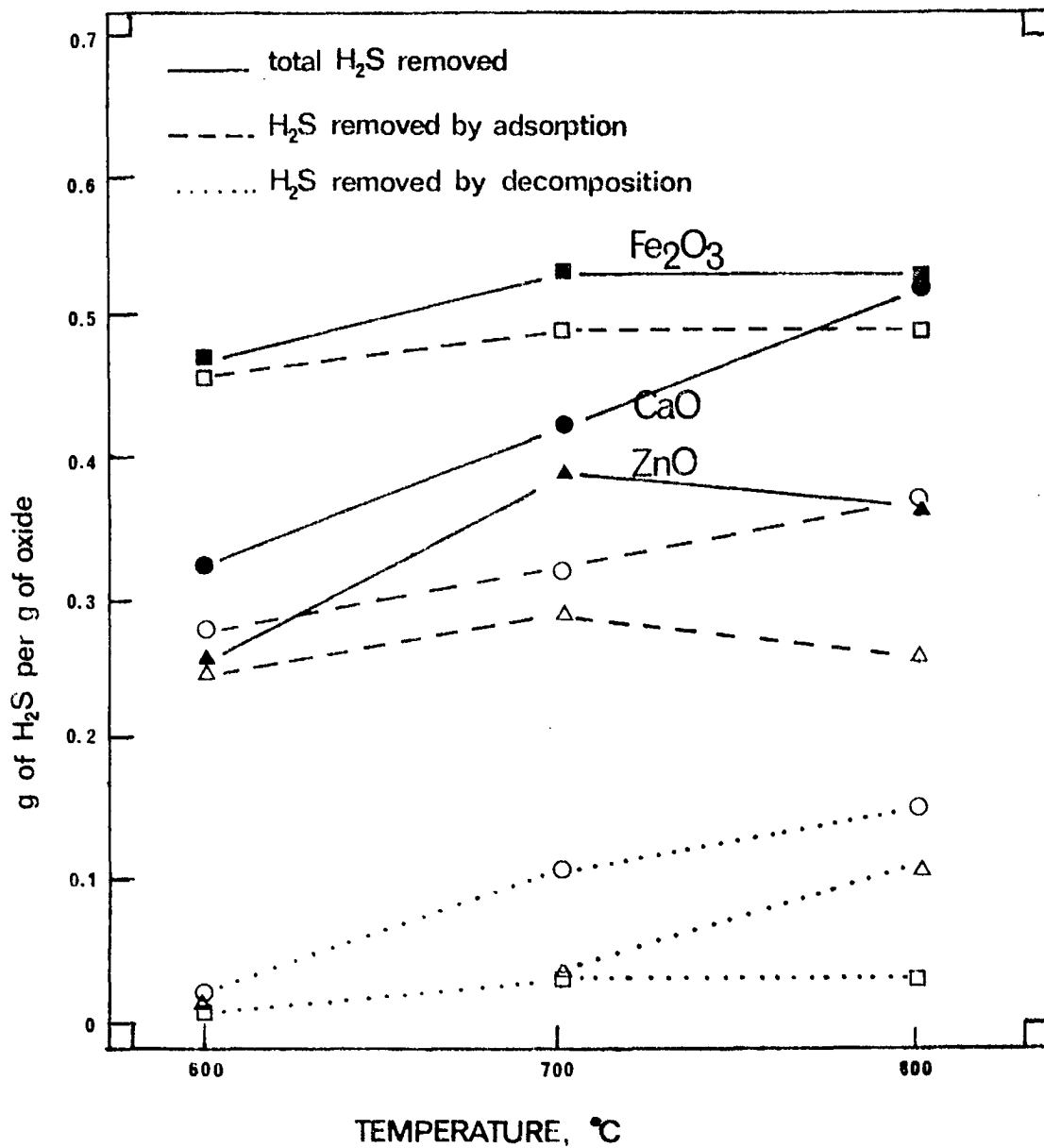
Adsorbent	Temperature °C	Content of S, determined	wt % stoich. of MeS
CaO	600	29.7	
	700	32.9	44.4
	800	35.0	
ZnO	600	25.9	
	700	26.1	32.8
	800	25.8	
Fe ₂ O ₃	600	36.5	
	700	36.8	36.4
	800	34.8	

Me = Ca, Zn and Fe

Captions to Figures

- Fig. 1 Concentration of H_2S and H_2 in exiting gas versus time at $700^\circ C$ in the presence of ZnO , CaO and Fe_2O_3 (2 g) (solid symbols for H_2S)
- Fig. 2 Effect of temperature on the amount of H_2S adsorbed and decomposed per one gram of oxides
- Fig. 3 Cumulative amount of H_2S (in grams per gram of oxide) either adsorbed or decomposed at 600° and $800^\circ C$ in the presence of CaO , ZnO and Fe_2O_3
- Fig. 4 Cumulative amount of H_2S (in grams per square meter of oxide) adsorbed at 600° and $800^\circ C$ in the presence of CaO , ZnO and Fe_2O_3





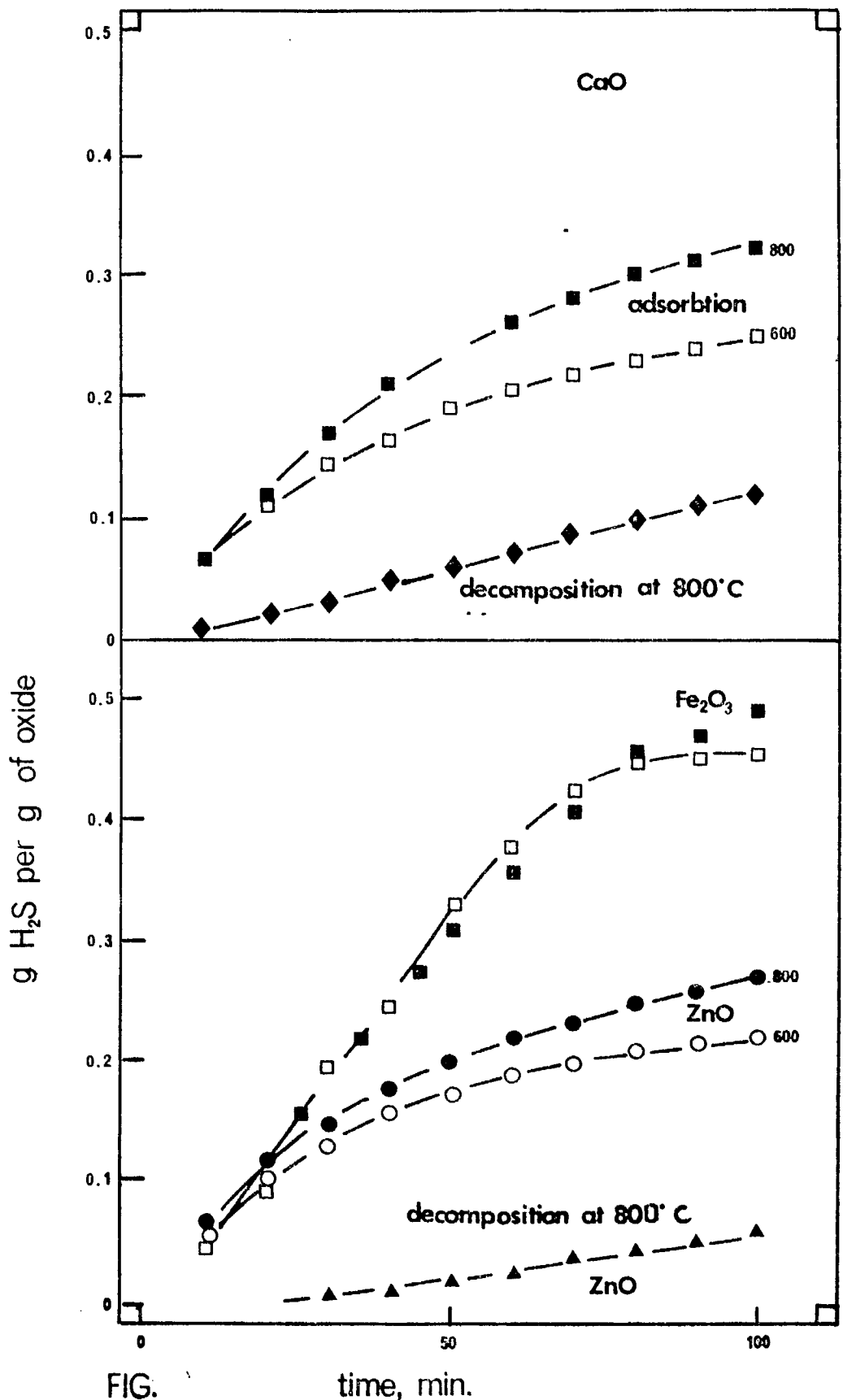


FIG.

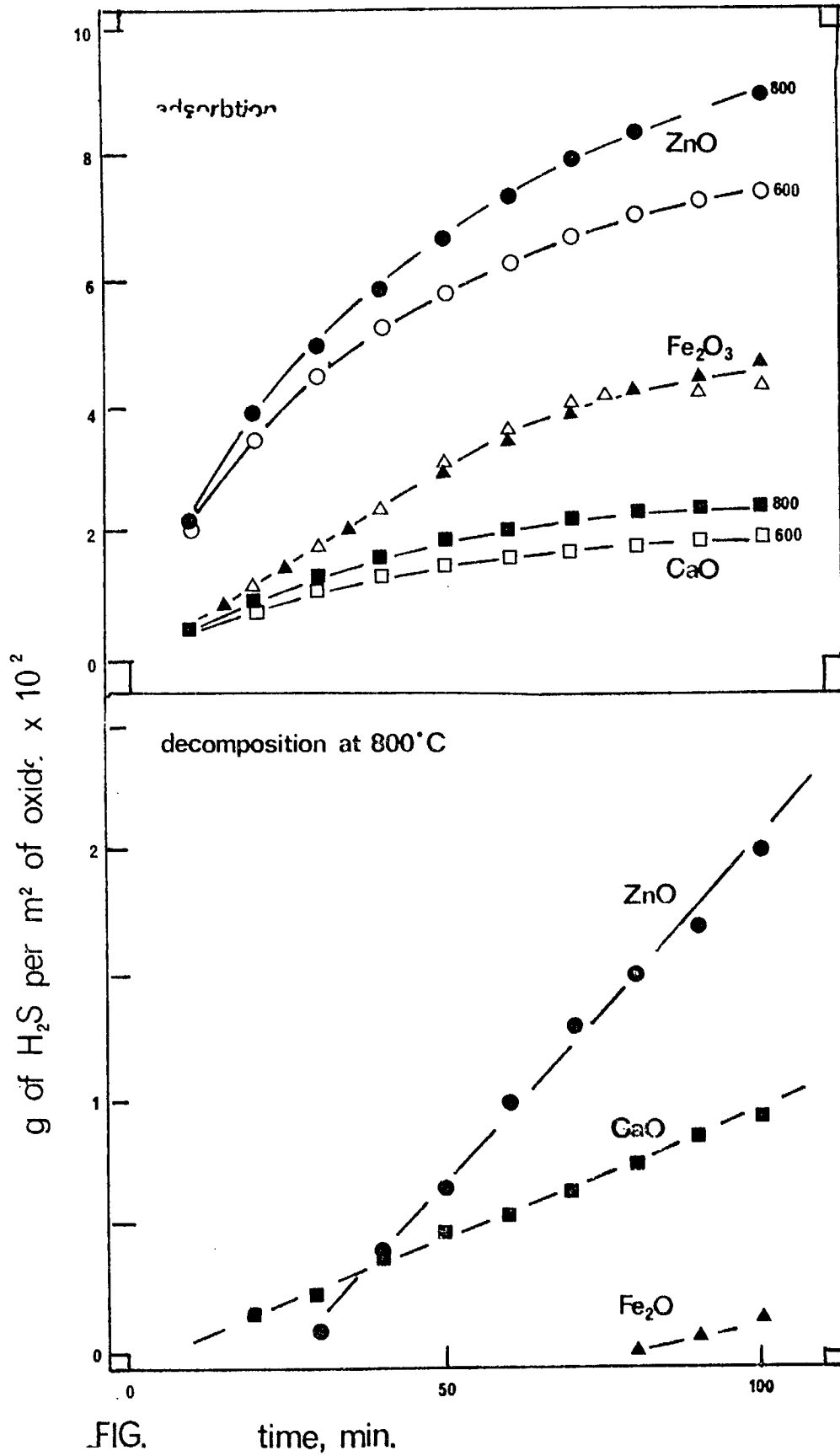


FIG. time, min.