

H_2S ADSORPTION AND DECOMPOSITION IN THE PRESENCE OF MANGANESE NODULES

by

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ABSTRACT

The sample of manganese nodule was tested as a potential adsorbent for H_2S removal from hot gas. In the first stage the H_2S was removed via its reaction with the adsorbent. After the complete sulphidation the adsorbent had catalytic effects on H_2S decomposition. In the temperature range of 600° to 800°C the amount of H_2S which reacted with one gram of the nodule per unit of time was temperature independent whereas that which decomposed showed a fivefold increase. The rate of H_2S reaction with the adsorbent and that of its decomposition was of the first and a half order, respectively, with respect to the amount of H_2S flowing through the reactor per unit of time.

The addition of 10 wt % of CaO to the manganese nodule had little effect on slope of gms of H_2S adsorbed/gms of nodule versus time and gms of H_2S decomposed/gms of module versus time correlations but increased the sulphur capacity of the adsorbent by about 30%.

INTRODUCTION

The combination of gasification and combustion (combined cycle) offers an alternative for power generation. The utilization of gasification products in this cycle requires the removal of particulates and corrosive species. On a commercial scale this step is performed at temperatures significantly lower than those of gasification. The cooling of gas is associated with heat losses, which affect thermal efficiency of the route. However losses could be avoided if purification was performed at near gasification temperatures.

Sulphur-containing compounds constitute the main portion of corrosive species. Under a reducing atmosphere, such as during gasification in a moving bed or in a fluidized bed in the presence of steam, most of the sulphur in the feedstock is converted to H_2S . The H_2S is also a byproduct of other coal processing, heavy oil upgrading and petroleum refining technologies.

The removal of H_2S from gaseous mixtures at high temperatures requires a contact with solid adsorbents. To be an efficient adsorbent a material must possess a high affinity for H_2S . In addition, the adsorbent must be resistant to reduction by H_2 and CO when purification of gasification products is considered. Thermodynamic calculations showed that among ten oxides, the oxides of Ca, Fe, Zn and Mn fulfill these requirements best (1). It was further confirmed that besides a high affinity for H_2S the adsorbent must possess a sufficient surface area (2).

Some of the oxides identified as efficient H_2S traps are frequently part of many naturally occurring clays and minerals. This prompted the search for materials with high content of these metals as much as a large surface area. From this point of view manganese nodules appear to be potential solids for the adsorbent preparation. For example, the Fe + Mn content in the nodules can be as high as 45 wt % and the surface area from 100 to 300 m^2/g (3).

EXPERIMENTAL

Materials

The Mn-nodule sample used in the present study was obtained from the Geological Survey of Canada. The sample was crushed and pelletized to 1.5 mm diameter and 1.5 mm high pellets. The pellets were used as the H_2S adsorbent without further pretreatment.

The CaO+Mn-nodule sample was prepared by impregnating the Mn-nodule using a solution of Ca nitrate. The slurry was then dried and pelletized.

The surface area of the sample, determined by N_2 BET was $101 \text{ m}^2/\text{g}$. The chemical composition of the sample is shown in Table 1.

Table 1 - Chemical composition of the Mn-nodule (wt %)

SiO_2	29.4
Al_2O_3	7.4
Fe_2O_3	42.6
TiO_2	0.4
P_2O_5	0.4
CaO	1.2
MgO	0.4
SO_3	1.4
Na_2O	1.9
K_2O	1.4
BaO	0.5
Mn_3O_4	3.3

The mixture of $N_2 + H_2S$ (10% vol of H_2S) of UHP grade was supplied by the Liquid Air Company.

Apparatus and Procedure

The experimental system consisted of a vertical reactor made either of Vycor glass (10 mm ID) or 316 stainless steel (20 mm ID). In the former, the pellets were supported in the middle of the reactor by a quartz wool, whereas for the steel reactor a distributor plate was placed in the middle of the reactor. The reactors were externally heated by a Lindberg furnace. The gas mixture entered the reactor at the bottom.

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

Prior to the experimental run, the reactor, loaded with pellets was heated to experimental temperature in a stream of N_2 . This temperature was maintained for another 30 min when the N_2 was replaced by a $N_2 + H_2S$ mixture, after which changes in the composition of the exiting gas were noted. At the end of the run the system was cooled in a stream of N_2 .

Analytical Procedure

The exiting gas was analyzed by a multicomponent on line mass spectrometer. This involved determinations of H_2S , H_2 and SO_2 in the mixture with N_2 . An adjoining data system provided composition printouts every 2 min.

The arrangement of the mass spectroscopy 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 the 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 analytical system could not determine accurately the H_2S in concentrations lower than 0.01% vol.

RESULTS AND DISCUSSION

A blank experiment performed at 800°C in the metal reactor confirmed a high level of H_2S decomposition. This was indicated by the large content of H_2 in the gas exiting reactor (broken line in Fig. 1). After about 50 min the decomposition levelled off, most likely due to the surface saturation by sulphur. It is believed that in the steady state the decomposition is catalyzed by the sulphided surface. This is in accordance with catalytic effects of sulphides of transition metals in H_2S decomposition observed by Nishizawa et al (4).

The patterns in concentration of H_2 and H_2S in exiting gas changed significantly in the presence of the adsorbent (Fig. 1). In this case 20 g of the adsorbent was used. Thus, the H_2S concentration in exiting gas was mostly below the detection limits of the mass spectroscopic system. Also, the yields of H_2 were relatively high confirming the H_2S decomposition. The increase of H_2S content in the gas entering the reactor from 2.9 to 10% resulted in a rapid increase of H_2 content in exiting gas. However, another 30 min lapse occurred before a rapid increase in H_2S concentration in the exiting gas

was observed. It is believed that at the point of rapid H_2S concentration increase a complete saturation of the adsorbent by sulphur was reached.

To avoid the interference of walls H_2S removal from hot gas was investigated in a Vycor reactor. In this case the H_2S decomposition was insignificant. Thus, during a blank run performed at $900^\circ C$ using the $N_2 + H_2S$ mixture containing 10% H_2S , concentration of H_2 in the exiting gas never exceeded 0.5%. The results shown in Fig. 2 were obtained in the presence of 2.0 g of the adsorbent, using the same $N_2 + H_2S$ mixture at 0.1 L/min. The H_2S and H_2 profiles shown in Fig. 2 are temperature dependent. At higher temperatures H_2S appeared in the exiting gas at later stages. This would indicate on a more efficient H_2S removal with increasing temperature. In view of the progress of a mass transfer front through the bed, a sharper mass transfer zone is formed at higher temperatures (5). The H_2S concentration then levels off suggesting that the stage of adsorbent saturation by sulphur is being approached. The trends in H_2 concentration in exiting gas confirm that H_2S decomposition increased with the increasing adsorbent saturation by sulphur. Subsequently the decomposition remained constant. The high content of Fe oxide, known to be readily sulphided in the adsorbent proves that its sulphided form is catalytically active in H_2S decomposition reactions (6). As one would expect the H_2S decomposition increased with increasing temperature as indicated by the four-fold increase in H_2 concentration when the temperature was increased from 600° to $800^\circ C$.

Experiments with the same $N_2 + H_2S$ mixture but at 0.05 L/min (Fig. 3) confirmed the observations made in Fig. 2. For example, two distinct regions of H_2S removal were observed. In the first the H_2S was removed via its reaction with the adsorbent and its concentration in the exiting gas was lower than the detection limits of the analytical system. As soon as the adsorbent began to approach the stage of saturation by sulphur, H_2S decomposition, measured by H_2 concentration in the exiting gas began to increase. In the steady state the H_2 concentration was higher than that during the experiment performed at 0.1 L/min. This is attributed to the longer contact time of H_2S molecules during the run at 0.05 L/min. Further, the longer time needed to saturate the adsorbent by sulphur is in accordance with smaller amounts of H_2S contacting the adsorbent per unit of time at 0.05 L/min compared to that at 0.1 L/min.

Cumulative loadings of H_2S (in grams) adsorbed and the amount of H_2S decomposed per one gram of the adsorbent are shown in Fig. 4. These results were obtained from such curves as shown in Fig. 2 and 3 using the stepwise integration by sections. The results shown in Table 2 were estimated from linear portion of curves.

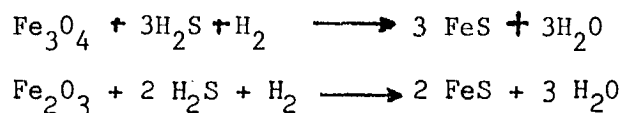
Table 2 - The amount of H_2S adsorbed and decomposed
(in grams of H_2S per gram of adsorbent per min)

Flow of H_2S L/min	Temperature °C	Adsorbed $\times 10^{-3}$	Decomposed $\times 10^{-4}$
0.010	600	6.4	2.3
	800	6.4	11.3
0.05	600	3.3	1.4
	800	3.3	7.1
0.02	800	1.4	4.5

The results in Table 2 confirm that the adsorption is directly proportional to the amount of H_2S flowing through the fixed bed of adsorbent, per unit of time. As one would expect the adsorption decreases and is almost equal to zero after the adsorbent saturation by sulphur is reached. This stage is attained earlier at higher H_2S flowrates.

Increasing temperature from 600° to 800°C had little effect on the initial rate of H_2S reaction with the adsorbent. This would suggest that Fe species play a major role in H_2S adsorption. Thus the log K values for H_2S adsorption by Fe_2O_3 and Fe_3O_4 in particular, exhibited the smallest change with temperature increase compared with several evaluated oxides (1). It has been established that FeS is the main product formed in reactions of H_2S with Fe_2O_3 based adsorbents (2,7). This suggests that some reduction of Fe_2O_3 occurs prior to its reaction with H_2S . In a reducing atmosphere such as is the case of H_2S containing hot gases the stable form of Fe oxides is Fe_3O_4 (8). In the present work the reduction of Fe_2O_3 to Fe_3O_4 aided by H_2S is supported by the presence of SO_2 in the exiting gas, e.g., at 600° and 800°C the SO_2 concentration was 0.05 and 0.12 % vol, respectively. Additional SO_2 was trapped via its reaction with basic species contained in the adsorbent (9).

The reduction of Fe_2O_3 to Fe_3O_4 could also occur with the aid of H_2 which was present in the exiting gas since early stages of the adsorption (Fig. 3). Then, the stoichiometric reaction of H_2S with Fe oxide may be written as follows:



It is known that H_2S reacts rapidly with Mn oxides (10) as well as with alkaline earth metal oxides (11). Similarly as in the case of Fe oxides the product of these reactions is MeS (Me is Fe, Mn or an alkali earth metal). These oxides participate in H_2S removing reactions though, in the present case, their contribution to the overall H_2S removal was much smaller than that of Fe oxides. A simple calculation, based on the content of active oxides in the adsorbent (Table 1) and the content of sulphur in the adsorbent at the end of the run (20.0 ± 0.2 wt %) confirms a near stoichiometric conversion to MeS . Such a high utilization of active oxides is attributed to very favourable surface structure of manganese nodules (3). For example, the surface area of the sample used in the present work was an order of magnitude higher than that of the adsorbent prepared from single oxides (2).

Cumulative amounts of H_2S (in grams) decomposed per gram of adsorbent increased linearly in the time intervals shown in Fig. 4. The rates of decomposition estimated from the slopes of lines are summarized in Table 2. Increasing the temperature from 600° to 800°C resulted in a fivefold increase in decomposition rate. In the H_2S flow range used a twofold increase of the flow resulted in a 1.6 fold increase of the H_2S decomposition rate.

The results in Fig. 4 suggest that H_2S decomposition begins to increase as soon as the adsorbent approaches the stage of complete saturation by sulphur. This would indicate that a sulphided form of Fe had catalytic effects on H_2S decomposition assuming that the Fe species in the adsorbent play the major role in H_2S removal from the hot gas, as observed by Nishizawa et al (4).

The level of H_2S adsorption exhibited some variation in the presence of Mn-nodule alone (saturation amount) as calculated by the Simpson's method (Fig. 4). For example, cumulative amounts of H_2S adsorbed before the saturation stage varied at different H_2S flows. However, as one would expect the content of sulphur in adsorbent determined at the end of each experiment

was identical, i.e., 20 ± 0.2 wt %, regardless of the flowrate of H_2S and temperature. These differences are attributed to the combination of uncertainties in the analysis of H_2S and measuring the flowrates.

The results in Fig. 4 further show that the addition of CaO (10 wt %) to the Mn-nodule had little effect on the initial adsorption and decomposition. However, the amount of sulphur required to saturate the adsorbent increased by about 30%. The combination of CaO with Mn-nodule resulted in an improved H_2S adsorbent suggesting that the addition of a compound having a high affinity for H_2S to naturally occurring materials having a large surface area may be a potential route for preparation of low cost adsorbents.

Experimental data suggest that the rate of H_2S removal from hot gas (R_R) in the presence of Mn-nodules can be expressed as the sum of rate of H_2S reaction with the adsorbent (R_A) and rate of H_2S decomposition (R_D), i.e., $R_R = R_A + R_D$. In the early stages the H_2S is removed entirely via its reaction with the adsorbent. As soon as the adsorption rate begins to level off the H_2 concentration in the exiting gas begins to increase indicating an increased H_2S decomposition. In the steady state no further adsorption occurs and H_2S removal from hot gas is governed by its decomposition.

The following simple expressions can be used to describe the rate of H_2S reaction and decomposition:

$$R_A = k_A [x] [a]$$

$$R_D = k_D [x] [d]$$

where k_A and k_D are apparent rate constants of H_2S reaction with the nodule and its decomposition; $[a]$ and $[d]$ are surface concentrations of reaction and decomposition sites, respectively and $[x]$ is the H_2S concentration in the hot gas entering the reactor. These expressions may be further simplified. Thus, at the initial stages the concentration of adsorption sites $[a]$ is the same for all experiments and the rates in Table 2 are very close to the initial rates. The same content of sulphur in adsorbent determined at the end of each run suggests that in the steady state the same level of adsorbent sulphidation was reached regardless of temperature and flowrate. Also, the concentration of decomposition sites $[d]$ may be similar for all experiments. With these assumptions the equations can be rearranged in the following manners:

$$R_A = k'_A [x]$$

$$R_D = k'_D [x]$$

where k'_A is a parameter reflecting the adsorption properties of an adsorbent while k'_D reflects decomposition properties of completely sulphided adsorbent, respectively.

The slope and the intercept of correlations of $\log R$ versus $\log [x]$ can be used to estimate reaction order and rate constants, respectively. Using the data in Table 2 for 800°C, the slope for the H_2S reaction with the adsorbent was 1.1 and for the H_2S decomposition reaction 0.5 indicating the first order kinetic of the former. This suggests that the total H_2S adsorption is controlled by the amount of H_2S flowing through the adsorbent bed. It is believed that H_2S decomposition requires a proper contact with the surface. In other words, more than one type of H_2S configuration with the surface may exist but only one, i.e., the activated, form will participate in decomposition reactions.

The antilog of intercepts yield the values of k'_A and k'_D . The former is the parameter, which may be used in a series of different adsorbents to determine relative efficiency for H_2S removal via its reaction with solid adsorbents. The k'_A and k'_D values estimated from the results obtained at 800°C were 7.1×10^{-3} and 2.8×10^{-3} , respectively. Using these values of the constants and the slopes estimated above the rate equation for H_2S removal at 800°C can be expressed as follows:

$$R_A = 7.1 \times 10^{-4} [x]$$

$$R_D = 2.8 \times 10^{-4} [x]^{1/2}$$

assuming the rates and H_2S concentrations in the units shown in Table 2.

In conclusion, the Mn nodule used in the present work appears to have properties considered desirable for a good H_2S adsorbent. It may be used alone or as its large surface area suggests, as a support combined with metals having a high affinity for H_2S . However, it is recognized that the surface structure of Mn nodules can be affected by thermal treatment (3). These aspects will be the subject of further investigations.

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CAPTIONS TO FIGURES

Fig. 1 - H_2S adsorption and decomposition in the metal reactor (20 g of Mn-nodule)

Fig. 2 - Concentration of H_2S and H_2 in exiting gas in Vycor reactor (2 g of Mn-nodule and 0.1 L/min of $N_2 + 10\% H_2S$)

Fig. 3 - Concentration of H_2S and H_2 in exiting gas in Vycor reactor (2 g of Mn-nodule and 0.05 L/min of $N_2 + 10\% H_2S$)

Fig. 4 - Cumulative amounts of H_2S adsorbed and decomposed in Vycor reactor (2 g of Mn-nodule, 0.1 L/min 800°C, solid symbols adsorption, open symbols decomposition).

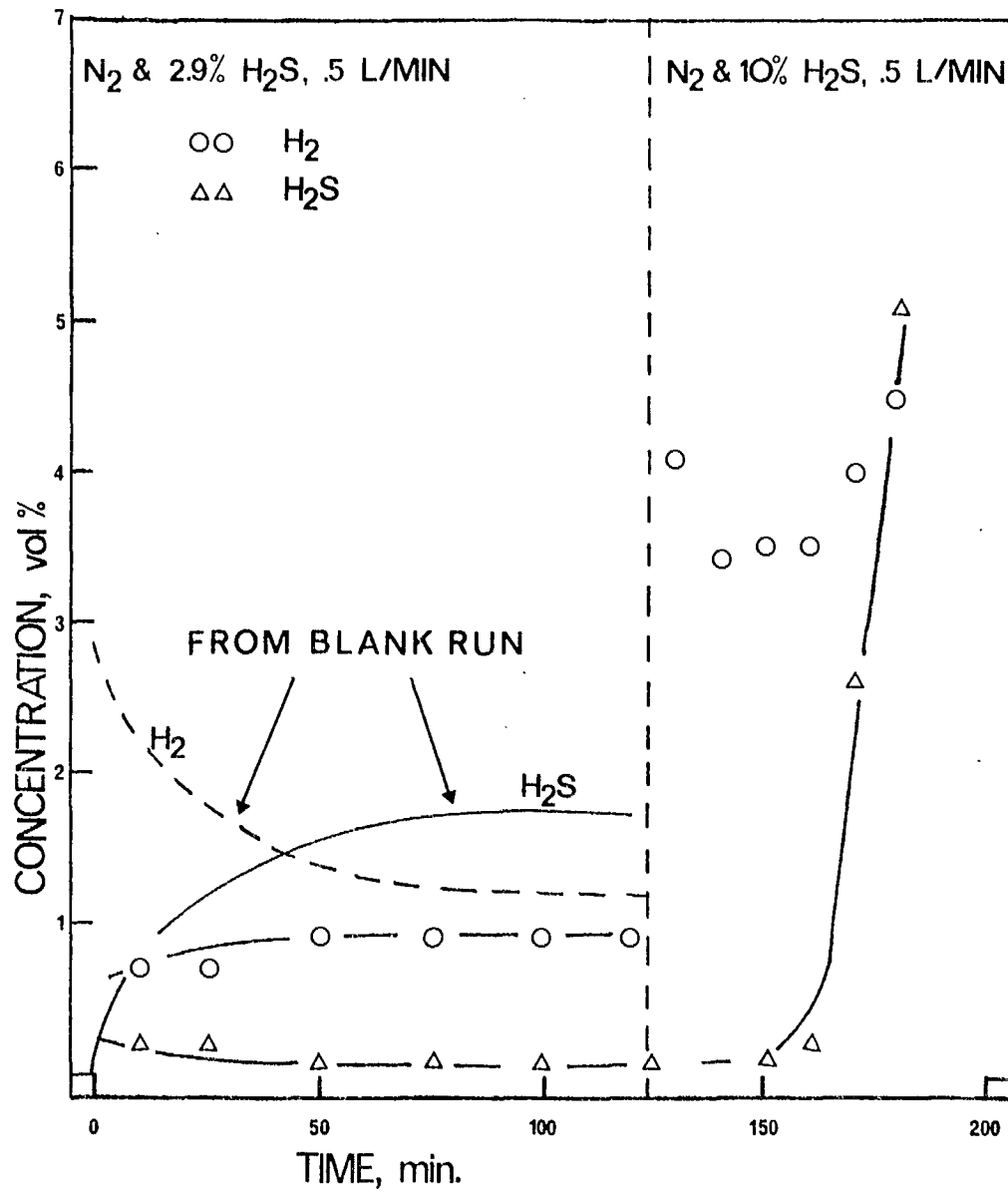


FIG. 1

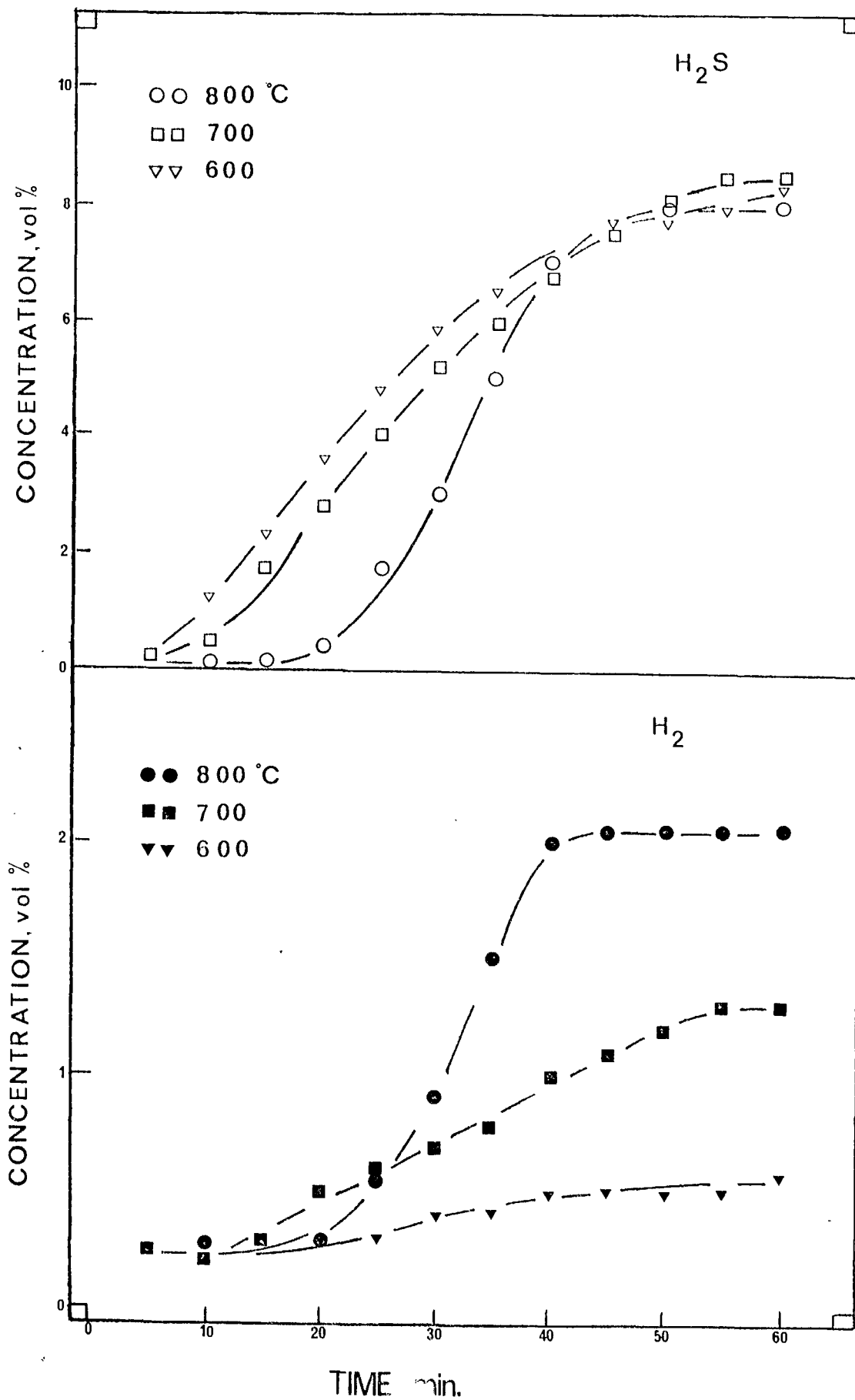


FIG. 2

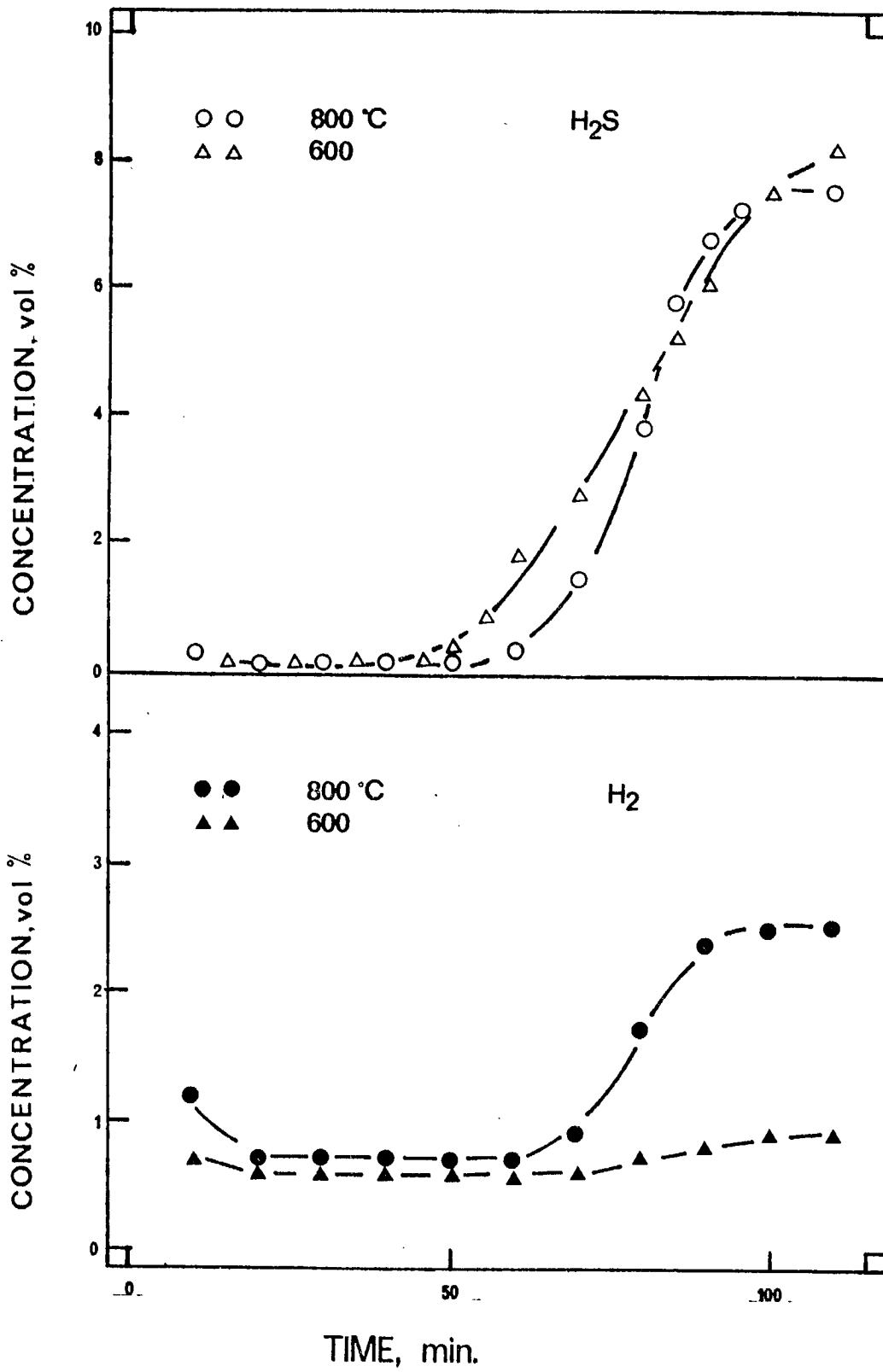


FIG. 3

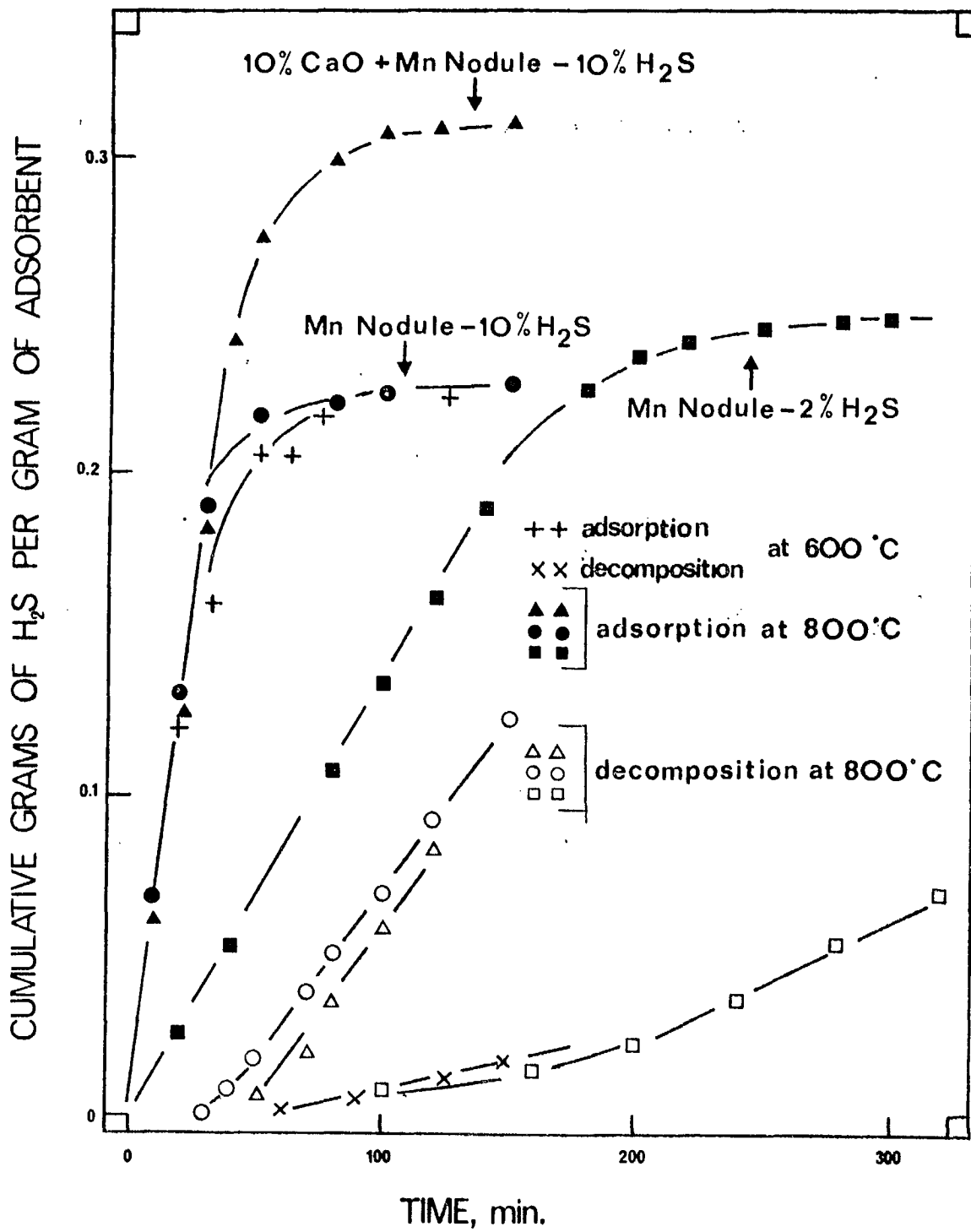


Fig. 4