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Enhancement of Sulfation of CaO by Fe_2O_3 in the Oxidative-Sorption Process for SO_2 Removal Using Fe_2O_3/CaO Binary Sorbents

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For the oxidative sorption of SO_2 using Fe_2O_3/CaO binary sorbents prepared by the usual impregnation method, reactivities and capacities for SO_2 removal have been investigated with TG measurements at temperatures near 500 °C in a stream of air containing SO_2 in concentration from 2 to 11%. Both the reactivities and the capacities of the sorbents were exceedingly enhanced by addition of Fe_2O_3 into CaO such small amounts as 0.1—0.8wt%, and further Fe_2O_3-loading over 1.0wt% resulted in a lowering in promoting effects. The changes in surface area and pore-size distribution with a variation of Fe_2O_3 content were also measured in order to discuss the correlation between chemical reactivity for SO_2 removal and physical property of the Fe_2O_3/CaO sorbents. In addition, Fe_2O_3-CaO mechanically mixed sorbents and the other binary sorbents such as Fe_2O_3/MgO or V_2O_5/CaO were tested to compare with the Fe_2O_3/CaO sorbents.

A large number of investigations has been made to develop process for waste gas desulfurization. Wet processes, such as alkali or limestone scrubbing, are being predominantly developed on a commercial scale. However, dry recovery processes are not always worthless since they would produce a usefull product and would avoid both flue gas reheating and the crystallization phenomena usually encountered in flue gas scrubbing.

In one of the dry recovery processes the waste gas is brought into contact with CaO or limestone, where upon SO_2 reacts with O_2 to produce $CuSO_4$ through the chemical reaction $SO_2+1/2O_2+CaO \rightarrow CaSO_4$.[1-3)] However, in the cases of these investigations, such high temperatures as 700—1000 °C are required to facilitate the desulfurization reaction.

It has been reported that chemical activation of the limestone sorbent can be achieved by the addition of small amounts of Fe_2O_3 into the limestone.[4,5)] These investigations were, however, made from the standpoint of practical technology for clean combustion of coal at the high temperature as 900 °C and the experimentals were not systematic.

In preliminary experiments, we have observed that Fe_2O_3/CaO sorbents exhibit high reactivities for SO_2 removal even at low temperatures near 500 °C. In this paper, details of the experimental results are reported together with a discussion of the relationship between chemical reactivity for SO_2 removal and physical property of the Fe_2O_3/CaO sorbents. In addition, we describe informations regarding Fe_2O_3-CaO mechanically mixed sorbents and the other binary sorbents such as Fe_2O_3/MgO or V_2O_5/CaO.

In this report, however, as a matter of convenience in experiments, sulfation tests of the sorbents were carried out by using the reactant gas containing SO_2 in

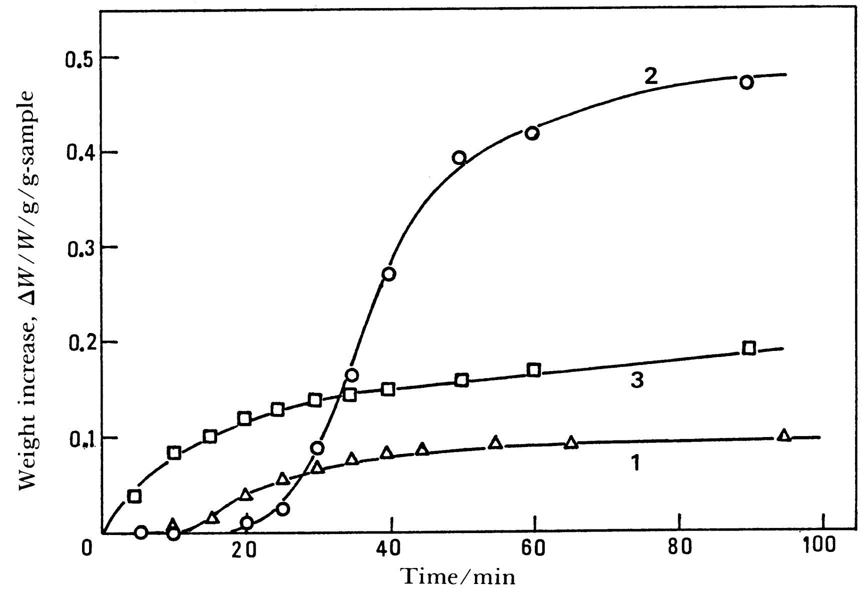

Fig. 1. Weight increase curves of various sorbents. 1: CaO, 2: Fe_2O_3 (0.11 wt%)/CaO, 3: Fe_2O_3 (0.95 wt%)/CaO. Reaction temperature: 500 °C, SO_2 concentration in the gas phase: 10.7%.

high concentration from 2 to 11%, instead of using such as a reactant gas with low concentration of SO_2 and with high concentration of CO_2 and H_2O as simulated combution gas.

Experimental

Materials. Commercial available powder of CaO reagent (Wako Pure Chemical Industries Ltd.,) was used as the sorbent after calcined at 500 °C for 2 h in a stream of air. The binary Fe_2O_3/CaO sorbent was prepared by the usual impregnation method: The prescribed mounts of $Fe(NO_3)_3$ aqueous solution were impregnated with the powders of CaO. The resulting mixture was air-dried at 120 °C, and calcined at 500 °C for 2 h in a stream of air. Several samples of Fe_2O_3/CaO sorbents differing the Fe_2O_3 content in the range of 0.1 to 3wt% were prepared by the same procedure. Mechanically mixed samples of Fe_2O_3–CaO were also prepared for the comparison with the Fe_2O_3/CaO samples prepared by the impregnation method. In the preparation of mechanically mixed Fe_2O_3–CaO sorbents, the measured amounts of Fe_2O_3, which was obtained by the calcination of $Fe(NO_3)_3$ at 500 °C, were throughly mixed with CaO powders by using agate mortar and pestle. The resulting mixtures were calcined again at 500 °C before use.

All the samples of sorbents used in this study were 12—20 mesh size. The other chemicals used were reagent grade and the gases were prepurified grade.

Apparatus and Experimental Procedure. The reactivity and capacity of various sorbents were measured in a TG reactor. The TG measurements were performed at 1 atm total pressure using a thermobalance equipped with quartz-spring which had a sensitivity of 50 μg. A small quartz boat with an area of about 1.3 cm^2 was used as the sample holder. About 200 mg of the sorbent sample was spread into a thin layer on the holder. The sample was heated to 500 °C in a stream of air and then allowed to stand for at least 30 min until there was no further weight loss. At the same temperature of 500 °C, the sufation reaction immediately followed in a flowing gas mixture of 10.7% SO_2 and the balance air, unless otherwise specified. Flow rates of the sulfating gas for the reaction were 170 ml (STP) min^{-1}, corresponding to a linear velocity of about 2 cm s^{-1}. The velocity was predetermined to be high enough to minimize gas-film diffusion resistance.

Results and Discussion

Time Course of Sulfation and Reaction Rates. Typical examples of weight increase with reaction time were illustrated in Fig. 1. Figure 1 indicates clearly that both the reactivity and the capacity of CaO reacting with SO_2 are appreciably increased by small amounts of Fe_2O_3 impregnated: CaO alone (curve 1) is usually very slow to react and its sulfation has an induction period of the order of 10 min. In contrast, CaO impregnated with about 1.0 wt% Fe_2O_3 (curve 3) is readily sulfated and there is no induction period. Fe_2O_3(0.11 wt%)/CaO sorbent (curve 2) exhibits a characteristic behavior that both the reactivity and the capacity for SO_2 removal are exceedingly enhanced by the impregnation of Fe_2O_3 such small amounts as 0.11 wt%, although the induction period has been elongated up to about 25 min.

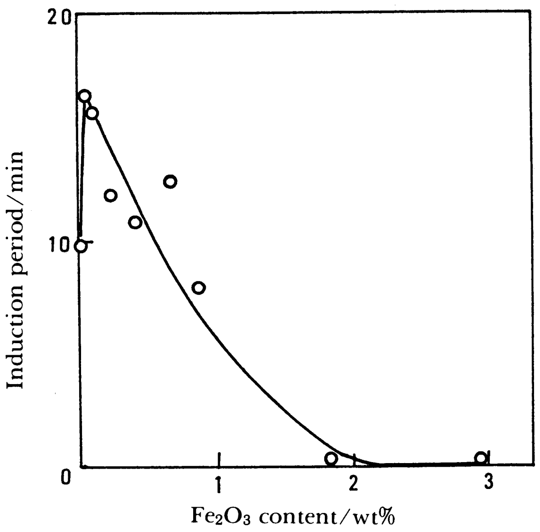

Fig. 2. Change in the induction period with Fe_2O_3 content.

As is shown in Fig. 2, the induction period in the sulfation reaction has been found to become progressively greater as the Fe_2O_3 content decreases, although the value shows some scatter. The reasons for occurrence of the induction period and for its mode of variation with the Fe_2O_3 content are still uncertain.

After the sulfation of sorbent was allowed to continue for about 100 min, X-ray diffractogram of the sorbent sample showed the pattern which was identified as those of the mixture consisting of CaO, $CaSO_4$, and Fe_2O_3. In addition, the X-ray diffractograms have proved that sulfated products such as $CaSO_3$ or $Fe_2(SO_4)_3$ are not present even in trace amounts. Thus we have tentatively speculated the reaction pathway of sulfation as the following consecutive steps:

$$SO_2\,(g) + 1/2\,O_2\,(g) \rightarrow SO_3\,(g) \tag{1}$$

$$SO_3\,(g) + CaO\,(s) \rightarrow CaSO_4\,(s) \tag{2}$$

where the oxidation step (1) of SO_2 proceeds catalytically over the surface of Fe_2O_3 and subsequent sulfation step (2) of CaO results in the formation of $CaSO_4$, accompanying weight increase in the sorbent sample.

In the weight increase-vs.-time relationship, the S-shaped curves have been observed in certain cases in which there are induction period between the start of sulfation process and the main acceleration of sulfation reaction. In these cases, the sulfation rates were varied complicatedly with the passage of time. Thus, the reactivities (the sulfation rates) were, for convenience, expressed in terms of the maximum slope of the TG measurement curves.

The sulfation rates (r) varied with SO_2 concentration of feed gas in such a way that the first-order kinetics can be roughly approximated on the basis of the data shown in Fig. 3.

Thus, it may be represented as

$$r = \left[\frac{d(\Delta W/W)}{dt} \right]_{max} = k'C_{SO_2} \tag{3}$$

where k'=apparent first-order rate constant (min^{-1} %$^{-1}$), C_{SO_2}=SO_2 concentration in the gas phase (%).

Effects of Fe_2O_3 Content upon the Sulfation. The reactivities of sorbents were extremely affected by the variation of Fe_2O_3 content. The rate constants k' calculated from Eq. 3 are shown in Fig. 4 as a function of the Fe_2O_3 content.

As is shown in Fig. 1, the weight increase during the course of sulfation depicts a steep rise within 90 min and then levels off. Thus, it can be accepted that the conversion of CaO into $CaSO_4$ beyond reaction times of 90 min is nearly equal to the maximum conversion being expected as the sulfation process of sorbent has been saturated. Figure 5 shows the dependence of the maximum conversion of CaO with the Fe_2O_3 content.

Figures 4 and 5 show a complete similarity of shape which tends to vary from sharp peak to rounded hump. From these results, it has been found that the Fe_2O_3 content favorable to rapid sulfation and large capacity for SO_2 removal lies in the vicinity of 0.3 to 0.7 wt%. The exact mechanism for such complicated changes in the reactivity and capacity with the Fe_2O_3 content is still not understood, however, we have tentatively speculated as follows: In the case of sorbent with a low Fe_2O_3 content below 0.3 wt%, the oxidation step of SO_2 over the surface of Fe_2O_3, Eq. 1 is a rate-limiting step in the reaction sequence and thus the over-all rate of sulfation is increased with an increase in the Fe_2O_3 content. In contrast, in the samples of sorbents with a high Fe_2O_3 content above 0.7 wt%, a rate-determining step is probably allowed to move from the catalytic oxidation step of SO_2 to the diffusion step of SO_2 or SO_3 through micro-pores of Fe_2O_3/CaO binary sorbent. The diameter of the micro-pores and/or the porosity of Fe_2O_3/CaO sorbent samples seem to be reduced with an increase in the amount of Fe_2O_3 coating surface of CaO sorbent, and subsequently a fraction of the entrances to a micro-pore is blocked with an additional deposition of Fe_2O_3 when Fe_2O_3/CaO sorbent is prepared by the impregnation method. Thus, the global rates in the sulfation of Fe_2O_3/CaO sorbents with a high Fe_2O_3 content is allowed to be rapidly lowered with increasing of the Fe_2O_3 content.

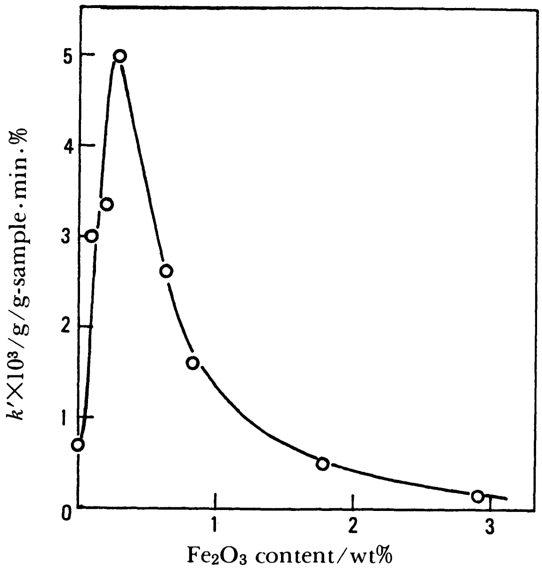

Fig. 4. Variation in rate constant k' at 500°C with Fe_2O_3 content.

The sulfation of CaO into $CaSO_4$ is well-known to be heterogeneous solid-gas reaction accompanying a change in volume of solid phase.[2] With the passage of

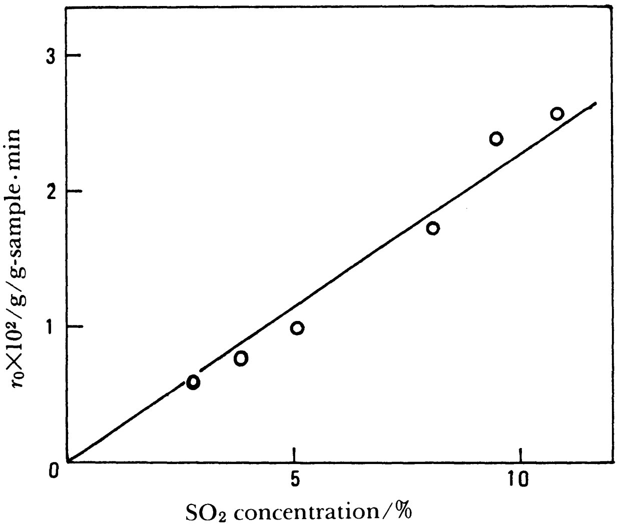

Fig. 3. Initial rates in the sulfation of Fe_2O_3 (0.11 wt%)/CaO as a function of SO_2 concentration in the gas phase. Reaction conditions are the same as for Fig. 1.

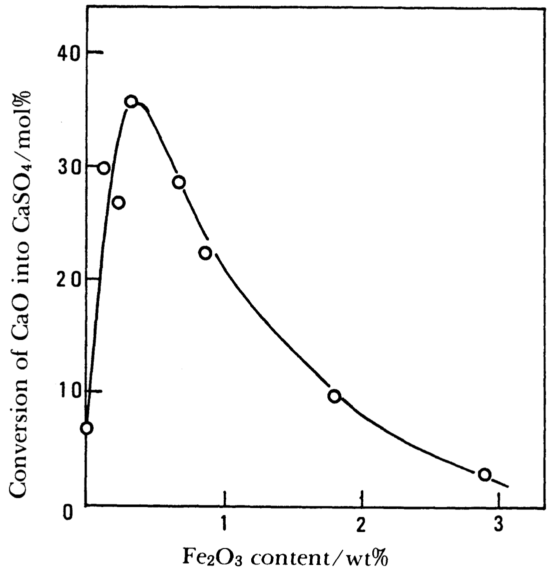

Fig. 5. Dependence of the maximum conversion of CaO with Fe_2O_3 content.

sulfation process the pore closing arises from the formation of product layer. The fraction conversion of CaO into $CaSO_4$ is ultimately limited, therefore, to the level of less than 40%, as is shown in Fig. 5.

Reactivities of Mechanically Mixed Fe_2O_3-CaO Sorbents. The sulfation experiments using mechanically mixed Fe_2O_3-CaO sorbents were separately conducted in order to compare with Fe_2O_3/CaO sorbents prepared by the impregnation method. The data of the rate constant and the conversion of CaO are shown in Fig. 6 as a function of Fe_2O_3 wt%. Figure 6 indicates that the data increase monotonically up to about 2 wt% of Fe_2O_3 content and then go up to a constant value. The shape of curves is simple and distinct clearly from such complicated curves shown in Figs. 4 and 5. However, the saturated values in both the rate constant and the conversion of CaO are close to the maximum values in Figs. 4 and 5, respectively. This fact suggests that the sulfation process proceeds consecutively through the catalytic oxidation step, Eq. (1), and the sulfation step, Eq. (2), as mentioned in the previous section. In addition, application of physically mixed Fe_2O_3-CaO sorbents is also anticipated to provide a simple and convenient method for SO_2 removal, although much larger quantities of Fe_2O_3 should be mixed with CaO in comparison with the case of sorbents prepared by the impregnation method.

Surface Area, Pore-Size Distribution and SEM-Photograph of the Sorbents Prepared by Impregnation Method. The change in surface areas of sorbents differing the Fe_2O_3 content was depicted in Fig. 7. The surface areas were determined by BET method using N_2 as the adsorbate. Figure 7 indicates that surface area of Fe_2O_3/CaO binary sorbent results in a steep rise in a very narrow interval of Fe_2O_3 content ranging from 0.1 to 0.2 wt% and then is allowed to decrease rapidly to about one-half its value in the Fe_2O_3 content of 1.0 wt% or more. The steep rise in surface area of Fe_2O_3/CaO sorbents with a low content of Fe_2O_3 is probably due to overlapping of the surface areas of CaO itself and Fe_2O_3 finely deposited on the surface of CaO. On the other hand, the decrease in surface area in the sorbents with a high content of Fe_2O_3 over 1.0 wt% is possibly ascribed to pore closing in micro-pores of CaO by the further deposition of much larger quantities of Fe_2O_3.

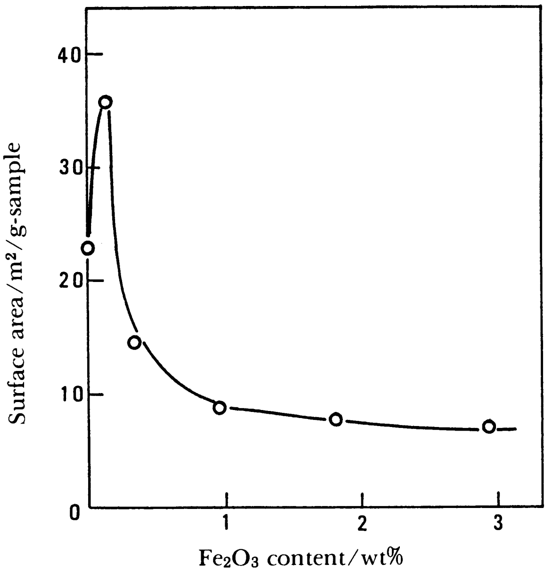

Fig. 7. Change in surface areas of Fe_2O_3/CaO samples with Fe_2O_3 content.

The pore-size distribution measured with a mercury porosimeter is shown in Fig. 8. From the data shown in Fig. 8, it can be speculated that deposition of Fe_2O_3 trends to shrink or clog smaller pores in preference to large pores.

The scanning electron microscopic (SEM) measurements of various sorbents have clearly demonstrated that, as the amount of Fe_2O_3 impregnated is increased, fine particles constituting of solid phase of

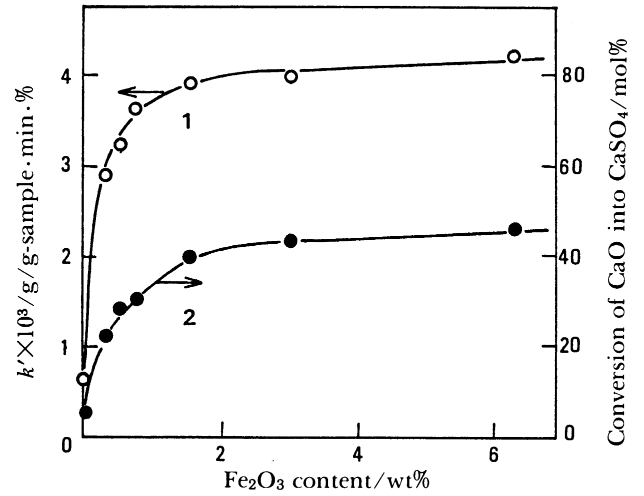

Fig. 6. Sulfation data relating to mechanically mixed Fe_2O_3-CaO samples. Reaction conditions are the same as for Fig. 1.

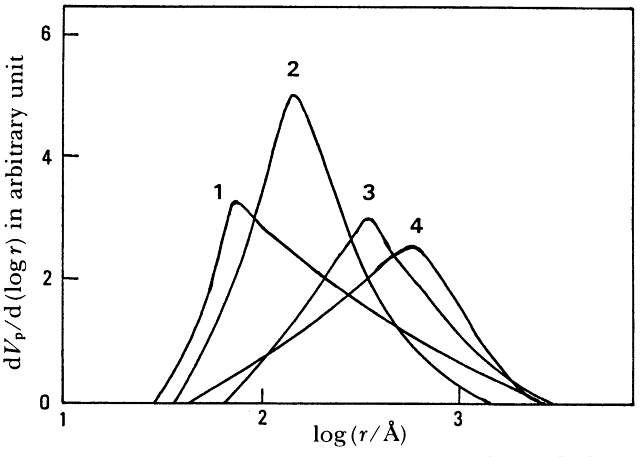

Fig. 8. Pore-size distribution in the samples. 1: CaO, 2: Fe_2O_3 (0.22 wt%)/CaO, 3: Fe_2O_3 (0.31 wt%)/CaO, 4: Fe_2O_3 (0.95 wt%)/CaO. r: pore radius in Å, V_p: pore volume.

sorbent become progressively greater in the range of about several microns to twenty microns. Similarly it has been revealed that the grain size of sorbent is allowed to appreciably enlarge by the product layer of sulfation reaction.

Other Promoters and Sorbents for Catalyzed Sulfation. In the previous sections, only the binary system consisting of Fe_2O_3 and CaO has been investigated as the sorbent. In this section, we will describe experimental results with respect to the other promoters and sorbents.

Various metal oxides such as V_2O_5, MnO_2, NiO, or CoO, other than Fe_2O_3, have been also loaded into CaO in the content of 0.3 wt% by the similar impregnation method as for Fe_2O_3/CaO sorbent. All of these oxides exhibited more or less the promotive action for catalyzed sulfation of CaO. The promoting action decreased in the order: $MnO_2 > V_2O_5 > Fe_2O_3 \gg NiO \cong CoO$. Two kinds of oxides, MnO_2 and V_2O_5, have catalytic properties somewhat superior to that of Fe_2O_3, however, application of these oxides must be avoided in the practical point of view and their high costs.

In analogy with CaO, alkaline earth oxides such as MgO or BaO are to be expected for a suitable sorbent. The sulfation tests using Fe_2O_3/MgO or Fe_2O_3/BaO have been made in order to compare their reactivities with that of Fe_2O_3/CaO.

The sorbent samples of Fe_2O_3/MgO or Fe_2O_3/BaO with a different Fe_2O_3 content were prepared by the similar impregnation method as that of Fe_2O_3/CaO. The commercial reagents of $Mg(OH)_2$ and $BaCO_3$ were used as the starting material in the preparation of the respective sorbent. These two powders of reagents were calcined at 500 °C for 2 h in a stream of air, and then were impregnated with the prescribed amount of $Fe(NO_3)_3$ aqueous solution. The resulting mixtures were hereinafter treated with the similar manner as that of the preparation of Fe_2O_3/CaO sorbent.

In the experiments used Fe_2O_3/MgO as the sorbent, the sulfation rates and the conversion of MgO into $MgSO_4$ were altered with the Fe_2O_3 content as shown in Fig. 9. Figure 9 indicates that both the rate constant k' and the conversion of MgO are lowered about one order of magnitude compared to the values of Fe_2O_3/CaO sorbent. In addition, it can be seen from Fig. 9 that capacities for SO_2 removal are increased monotonically with a low ratio by increasing Fe_2O_3 content. These facts seem to be due to poor chemical reactivity of MgO with SO_3 to the formation of $MgSO_4$. In the sulfation reaction using Fe_2O_3/MgO sorbents, the induction period was completely missing and this was also distinct from the cases of Fe_2O_3/CaO sorbents.

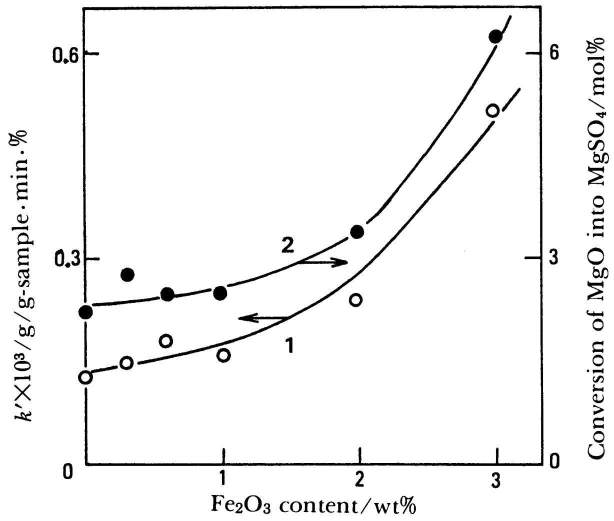

Fig. 9. Sulfation data relating to Fe_2O_3/MgO samples. Reaction conditions are the same as for Fig. 1.

The reactivities and the capacities for SO_2 removal of Fe_2O_3/BaO or Fe_2O_3/SrO sorbents were substantially comparable to that of Fe_2O_3/MgO. Consequently, the adoptability of sorbents for SO_2 removal can be summarized as $Fe_2O_3/CaO > Fe_2O_3/MgO \cong Fe_2O_3/SrO > Fe_2O_3/BaO$.

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