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# STUDIES ON THE MECHANISM OF REACTION BETWEEN SULFUR AND OXYGEN ON A MOLYBDENUM SURFACE BY MEANS OF AUGER ELECTRON SPECTROSCOPY

## ---- THE WORKING STATE OF THE CATALYST SURFACE ----

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A direct observation of the "working state of the catalyst" by Auger Electron Spectroscopy during the reaction between segregated sulfur and gaseous oxygen on molybdenum revealed that the reaction takes place through the direct interaction between the ambient oxygen molecules and the surface sulfur at lower temperatures, whereas it proceeds predominantly between the sulfur and the chemisorbed oxygen at higher temperatures.

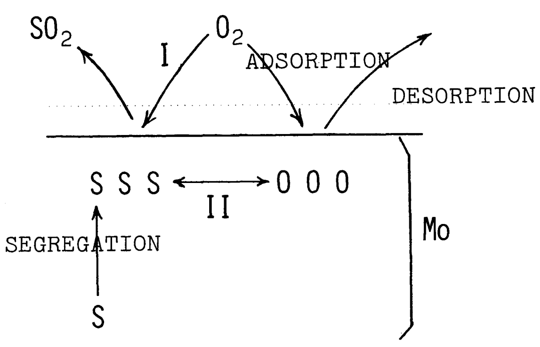
The newly developed Auger Electron Spectroscopy(AES) has many advantages for studying the solid surface phenomena, such as adsorption,segregation or changes in the surface composition and also for examining the cleanliness of the surface, because of its high sensitivity in the elemental analysis of the surface composition.

The first successful direct observation of the "working state of the catalyst surface during the reaction" by AES will be reported in the reaction between segregated sulfur and gaseous oxygen on a molybdenum surface. The behaviors of all the surface species, not only sulfur but also oxygen and molybdenum, were studied under the reaction. The overall reaction was experimentally separated into several elementary processes by using "non-steady state method", each of them being investigated independently to elucidate the role they play in the overall reaction.

The AES data were obtained with the Simpson-Kuyatt type high resolution electron spectrometer, consisting of a hemispherical 180° energy analyzer with retarding electrostatic lenses.1)(primary electron energy; 1.3keV, incident and scattering angles; 27° each). The specimen was 99.96% molybdenum foil(3.2x6x0.015mm) obtained from H.Cross Co. Ltd. When it was heated electroresistively in vacuo($1\times10^{-7}$Torr) between 700-1300°C which was determined by pyrometer, sulfur appeared on the surface. By this procedure only sulfur segregated on the surface from the bulk above 700°C. The reaction between the sulfur thus segregated and the oxygen introduced into the system from $1\times10^{-8}$ to $2\times10^{-6}$Torr was studied in the temperature range between 700 and 1300°C. The rate of the segregation was much slower than the reaction rate at lower temperatures. The peak to peak intensities of the differentiated Auger spectra of sulfur, oxygen and molybdenum were used to estimate the amount of these elements on the surface to follow the behavior in the surface. The concentration of the surface species is proportional to the peak intensity within the first layer.2)3)(Sulfur peak was about 1.3 times as strong as that of molybdenum for the first sulfide layer, that was confirmed by the adsorption measurment of ammonia. All the reactions were carried out over this optimum surface.)

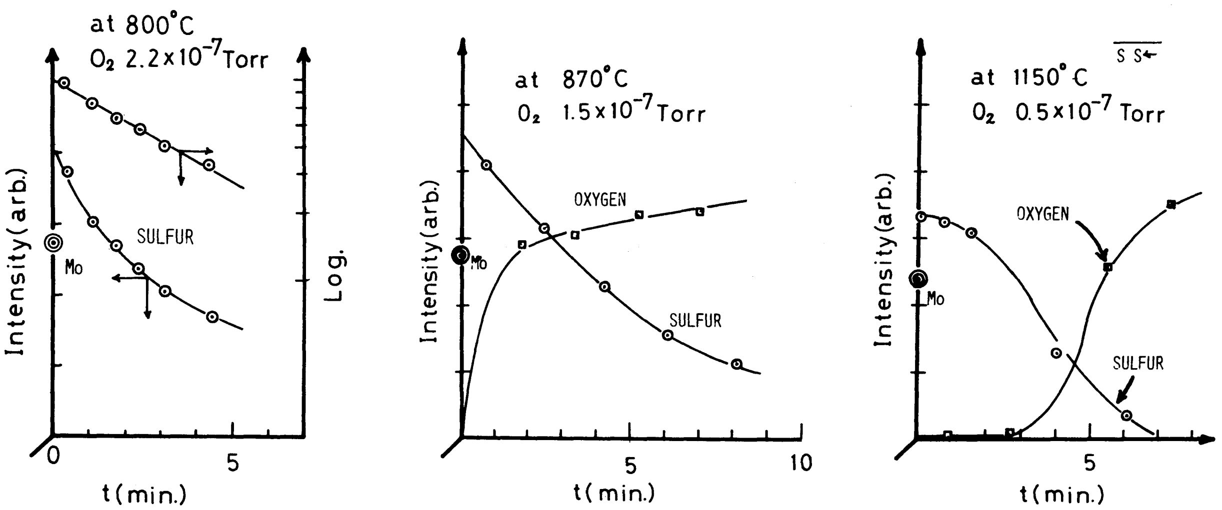
The overall reaction between the segregated sulfur and oxygen may take place through several steps such as, for instance, direct interaction of the ambient oxygen molecules with the surface sulfur (I) , oxygen adsorption, migration and reaction with the sulfur (II) and the desorption as $SO_2$.(Fig.1) The main purpose of this work is to determine the dominant reaction process, through which the reaction proceeds.

Fig. 1



The overall reaction to remove sulfur by gaseous oxygen was investigated with the AES measuring the changes in the concentrations of sulfur and oxygen on the surface with time after a sulfur rich surface had been prepared.(Fig.2) At lower temperatures around 700-800°C, sulfur decreased exponentialy with time and its rate was exactly proportional to the oxygen pressure. Consequently, the rate is expressed as follows; $dS/dt=-k(S)(O_2)$. At higher temperatures around 1200°C, on the other hand, it is significantly different from that at lower temperatures and autocatalytic decay was exhibited as given in Fig.2. The oxygen pressure dependence deviated from the first to the lower order at higher temperatures, though it approached to the first order as $O_2$ pressure was increased.

Fig. 2

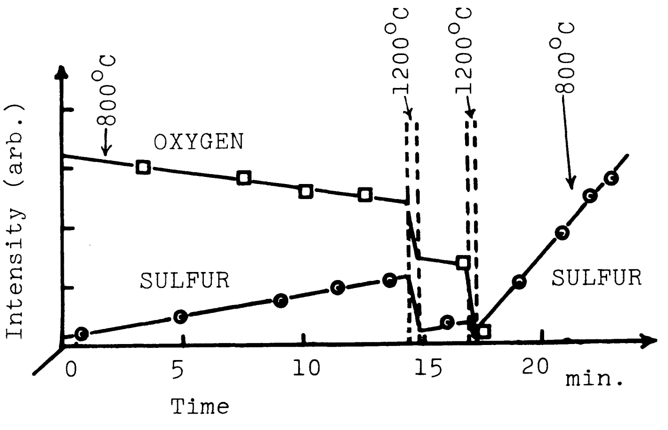


The behavior of the oxygen during the reaction was markedly influenced by the presence of sulfur. Although the adsorption of oxygen on the clean surface is readily completed even at $10^{-8}$Torr, the oxygen adsorption was observed on the sulfur segregated surface after a considerable induction period at higher temperatures. At lower temperatures , as given in Fig.2, the oxygen peak grew from the beginning as the reaction proceeded and both sulfur and oxygen coexisted on the surface during the reaction, whereas at higher temperatures the oxygen peak was observed only when sulfur on the surface was mostly consumed.(induction period for oxygen appearance) Sulfur and oxygen could not coexist in stable states at higher temperatures. These phenomena indicate that at higher temperatures the oxygen on the catalyst was rapidly cosumed by the sulfur such that oxygen does not appear on the surface until most of the surface sulfur is consumed.

These two different mechanisms were separately studied experimentally by non-steady state method in the following manner. When gaseous oxygen in the system was rapidly evacuated in the course of the reaction at 750°C, the sulfur removal from the surface stopped correspondingly although the oxygen on the molybdenum remained unchanged coexisting with the sulfur. The main part of the overall reaction at lower temperatures, accordingly, does not proceed between the adsorbed oxygen and sulfur, but with direct interaction with the ambient oxygen molecules,(process I). The rate equation and the behaviors of the surface species at this temperature may be reasonably interpreted with this mechanism. The sulfur and oxygen on the surface, on the other hand, react very slowly in the absence of ambient gaseous oxygen. When the reaction temperature was jumped from 800°C to 1200°C for a few second in the absence of oxygen(Fig.3), the surface reaction proceeded rapidly between the sulfur and oxygen and both elements readily decreased to have a clean surface, which was followed by the segregation of sulfur after the surface reaction was over. These phenomena and the induction period for the oxygen appearance in the working state indicate that the surface diffusion and the reaction between sulfur and oxygen are extremely rapid at higher temperatures and that the reaction between the chemisorbed oxygen and sulfur plays a predominant role in the overall reaction (process II).

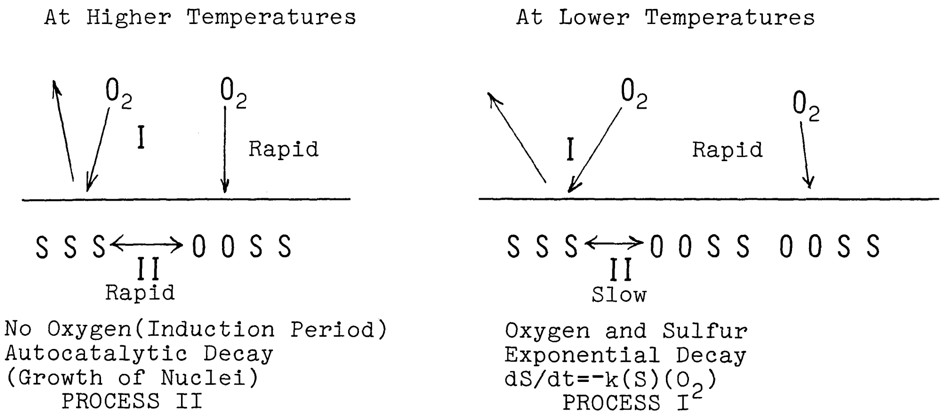
The Arrhenius plot of the overall sulfur removal reaction exhibited a break at about 900°C(this temperature is dependent on the $O_2$ pressure), the activation energy being 26 kcal and 10 kcal at higher and lower temperatures,respectively. The value of the activation energy at higher temperatures is the same as that of the segregation of sulfur separately determined by the AES. Those results suggest strongly that the overall reaction consists of two different mechanisms, processes I and II, and at higher temperatures the diffusion controlled process II becomes dominant because of its large activation energy.

Fig. 3



The scheme of the reaction is summarized in Fig.4. ----- The overall reaction consists of two different processes I and II, competing each other. At lower temperratures the process I is predominant, in which the reaction occurrs between the surface sulfur and the ambient oxygen. The reaction between sulfur and the adsorbed oxygen is not so rapid such that they coexist on the surface. At higher temperatures near 1200°C, on the other hand, the surface diffusion becomes rapid because of its large activation energy, and the process II becomes dominant in which the reaction proceeds via diffusion of sulfur and adsorbed oxygen. These two surface species, sulfur and oxygen, therefore, cannot coexist under the reaction conditions in stable states. The autocatalytic type reaction pattern at higher temperatures was satisfactorily interpreted with such mechanism.

Fig. 4



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