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# **SURFACE COMPOSITION OF DOUBLY AND TRIPLY PROMOTED IRON CATALYSTS FOR AMMONIA SYNTHESIS STUDIED BY MEANS OF ELECTRON MICROPROBE AUGER SPECTROSCOPY**

By

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## **Synopsis**

The surface composition of doubly and triply promoted iron catalysts for ammonia synthesis has been studied by means of electron microprobe Auger spectroscopy, and the non-uniform distribution of each of the catalyst components as well as nitrogen adsorption on the surface was demonstrated on the reduced catalysts after heating in the mixture of nitrogen and hydrogen. The intensive concentration of promoters at the surface was demonstrated and the state of the promoters such as aluminium at the surface is suggested to be in the form of their oxides. The segregation of sulfur at the surface was also demonstrated.

It was demonstrated that alumina inhibits the nitrogen chemisorption for the synthesis, supporting the view that alumina decreases the specific activity of the catalyst, but increases its total surface area preventing sintering.

## **Introduction**

Most of the industrial catalysts are multi-component systems and, in many cases, their surfaces are not uniform, having different composition or activity at different points in the surface. It is accordingly very important to study the distribution of not only each of the components, but also the catalytic activity or adsorbability in the surface. The study of the overall composition is, in this sense, not enough to examine the behaviour of catalyst surface,<sup>1)</sup> but needs more careful examination in detail.

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As to the ammonia synthetic promoted iron catalysts, so many researches have been carried out by many investigators with various techniques and the role of promoters has been studied, but we have still many problems left unsolved on this matter.

### Experimental

An electron microprobe Auger spectrometer (EMAS) was constructed which has a spatial resolution less than one micrometer.<sup>2)</sup> The dead space of the apparatus was approximately 100  $\ell$ . The catalysts were prepared as follows if not specifically described: A block of sintered unreduced promoted catalysts ( $5 \times 5 \times 1$  mm) (doubly promoted catalyst;  $\text{Fe}_3\text{O}_4$  96 wt%,  $\text{K}_2\text{O}$  1 wt%,  $\text{Al}_2\text{O}_3$  3 wt%: triply promoted catalyst;  $\text{Fe}_3\text{O}_4$  94 wt%,  $\text{Al}_2\text{O}_3$  4 wt%,  $\text{K}_2\text{O}$  1 wt%,  $\text{CaO}$  1 wt%) for industry obtained from the National Chemical Laboratory for Industry in Tsukuba was cut into thin slices and reduced in hydrogen gas (500 torr) stream at  $350 \sim 500^\circ\text{C}$ , collecting the water formed by a dry ice methanol trap for 9 days in a separate apparatus. The sample thus treated was quickly transferred to EMAS apparatus through the air. The reduced catalyst was further treated in hydrogen or ammonia in the EMAS apparatus.

The distributions of each of the components in the surface of the slices of doubly and triply promoted iron catalysts for ammonia synthesis have been studied and those of nitrogen adsorption and its reduction to ammonia, and also ammonia decomposition were studied under various conditions.

The quantitative estimation of the relative concentration of each of the surface elements is a complicated problem, but if we just divide each of the peak intensity by its cross section (3) for the Auger Process in the case of the third spectrum in Fig. 1, taking the different escape depth of their Auger electron into consideration, the relative concentration (in atom percentage) of each of the surface elements could be very roughly estimated.

### Results and Discussion

The sliced triply promoted catalyst reduced in a separate apparatus was transferred to the EMAS apparatus and then treated with hydrogen or ammonia. The Auger electron energy spectra, or the average composition of the surface, of those samples treated in hydrogen (10 torr) at  $500^\circ\text{C}$  for 26 hr and then in ammonia (20 torr) at  $450^\circ\text{C}$  for 16 hr in a static system are given in Fig. 1 with that of unreduced sample. A similar experiment was carried out for doubly promoted catalyst. It is easily confirmed in the figure that the promoters such as K, Al and Ca are intensively concentrated

## Surface Composition of Iron Catalysts

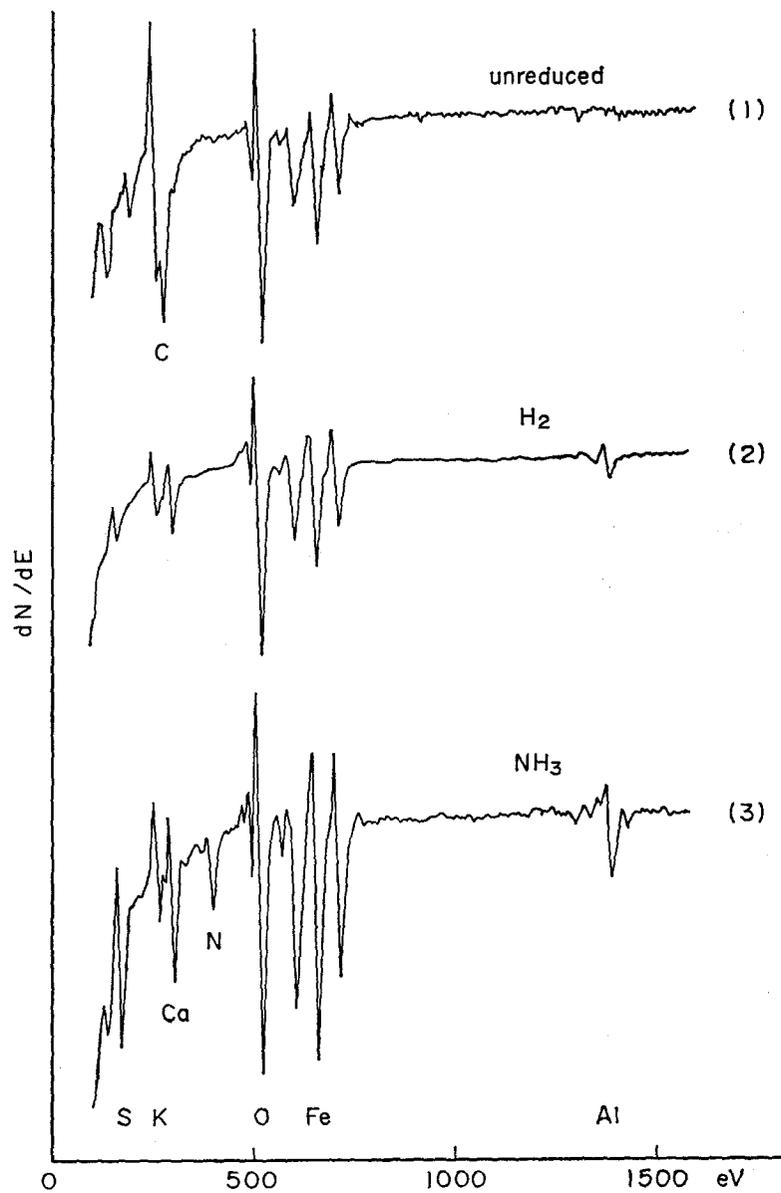
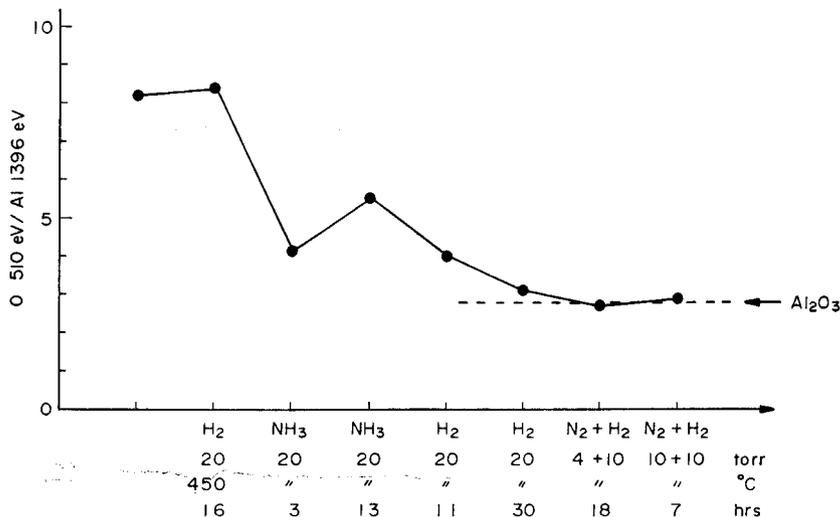


Fig. 1. Auger electron spectra of a triply promoted iron catalyst before<sup>1)</sup> and after<sup>2)</sup> hydrogen reduction and ammonia treatment.

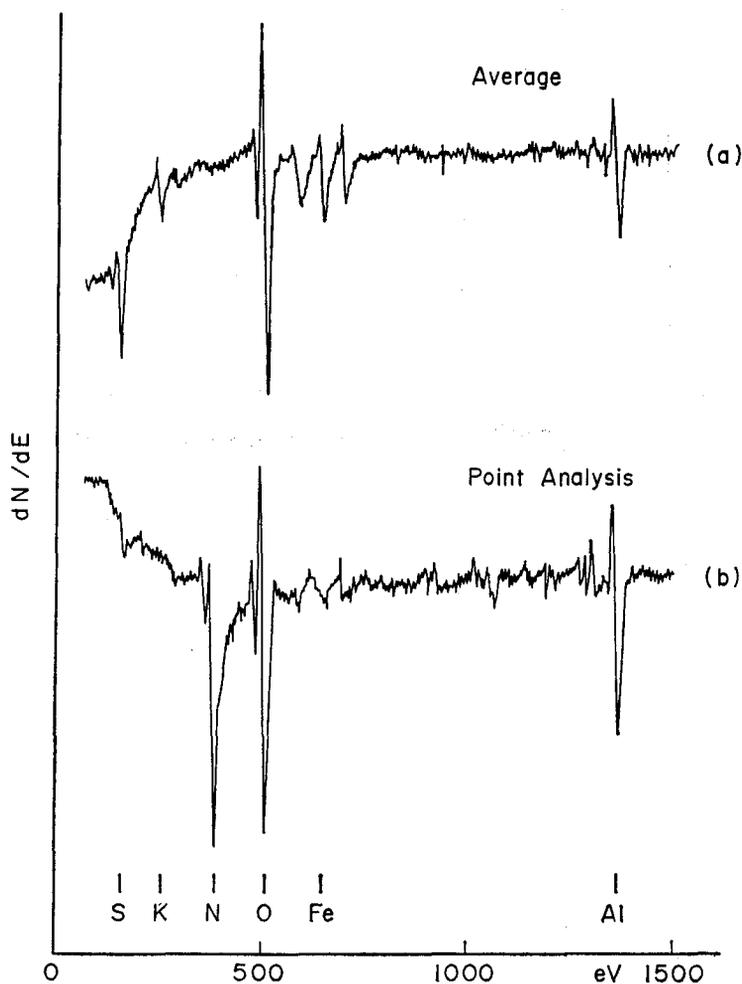
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**Fig. 2.** The ratio of the intensity of O (510 eV) peak to that of Al (1396 eV) for the doubly promoted iron catalyst are plotted as the reduction proceeded.

at the surface of the slice during the process of reduction and no Si was detected in the spectra. Another marked observation is the concentration of sulfur impurity at the surface, which also takes place in general in many other metals through its segregation from the bulk. The process of the reduction of unreduced doubly promoted catalyst has been studied in the EMAS apparatus in a batch system. The ratio of the intensity of O (510 eV) peak to that of Al (1396 eV) is plotted as the reduction proceeds in Fig. 2, where it is demonstrated that it approaches a constant value of 2.7, as the reduction proceeds, which is approximately the value for  $\text{Al}_2\text{O}_3$ . Such an observation strongly suggests that aluminium at the iron surface is in the state of alumina after the reduction.

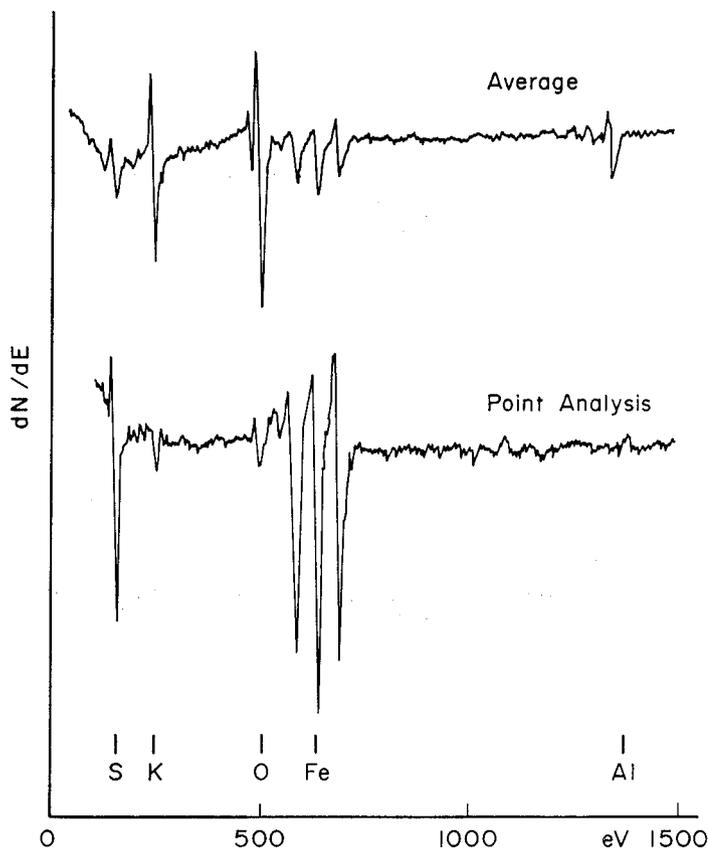
It is clearly shown from the SEM (scanning electron microscope) image that the catalyst surface is not uniform and many cracks appeared after the reduction. The Auger point analyses of several small parts in the surface of the well-reduced doubly promoted catalyst clearly showed that the surface was quite heterogeneous in its composition. Fig. 3 shows a result of Auger analysis of the overall (average) surface composition obtained by scanning a primary electron beam ( $0.8 \text{ mm} \times 0.8 \text{ mm}$ ). After treating the sample by  $\text{N}_2$  (10 torr) and  $\text{H}_2$  (10 torr) at  $450^\circ\text{C}$  for 7 hr in the EMAS. A characteristic result of point (about  $1 \mu\text{m}^2$ ) analysis where nitrogen is particularly concentrated is given in Fig. 3(b), although most of the places in the surface

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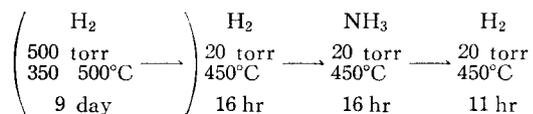


**Fig. 3.** A typical example of a characteristic point where nitrogen is particularly concentrated on a doubly promoted catalyst, although the overall concentration exhibits no nitrogen.

gave Auger spectra similar to that in Fig. 3(a). It is to be noted that, as shown in Fig. 3(a), the Auger peaks of sulfur, potassium, oxygen, iron and aluminium were observed moderately in the average composition of the surface, whereas no Auger peaks of nitrogen were observed, but at a limited part of the surface nitrogen is particularly densely adsorbed as given in Fig. 3(b). Such nitrogen could be removed by treating with hydrogen. In this manner it was demonstrated that the sites for the nitrogen adsorption as well



**Fig. 4.** Iron sulfide formation on a reduced doubly promoted iron catalyst exhibited by EMAS. The catalyst was reduced as follows:

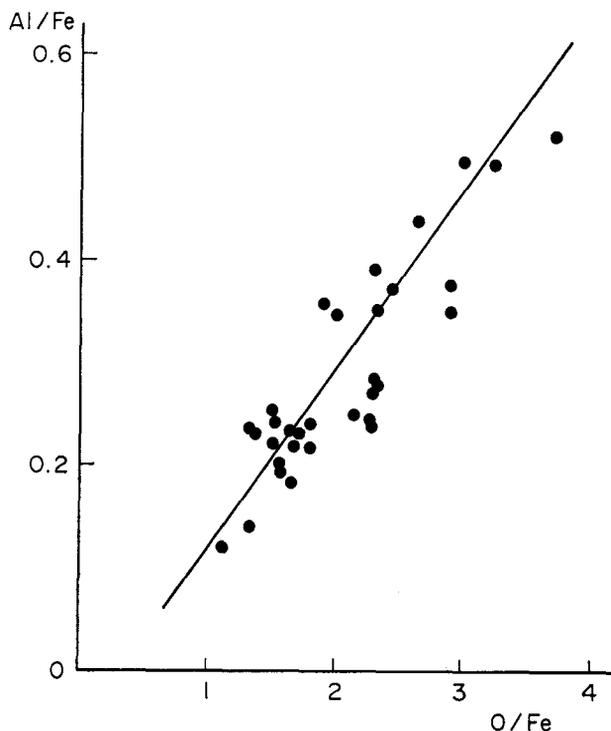


as ammonia synthesis are heterogeneously distributed in the catalyst surface.

It was also demonstrated by the point analysis that some parts of the catalyst surface are almost completely iron sulfide as given in Fig. 4. The sulfur segregated at the surface forms iron sulfide almost completely excluding all the other elements such as promoters.

The intensities of the Al peaks of point analyses are plotted against those of O peaks of triply promoted catalyst at many different points in the surface as given in Fig. 5. Similar plots for Ca are shown in Fig. 6. These

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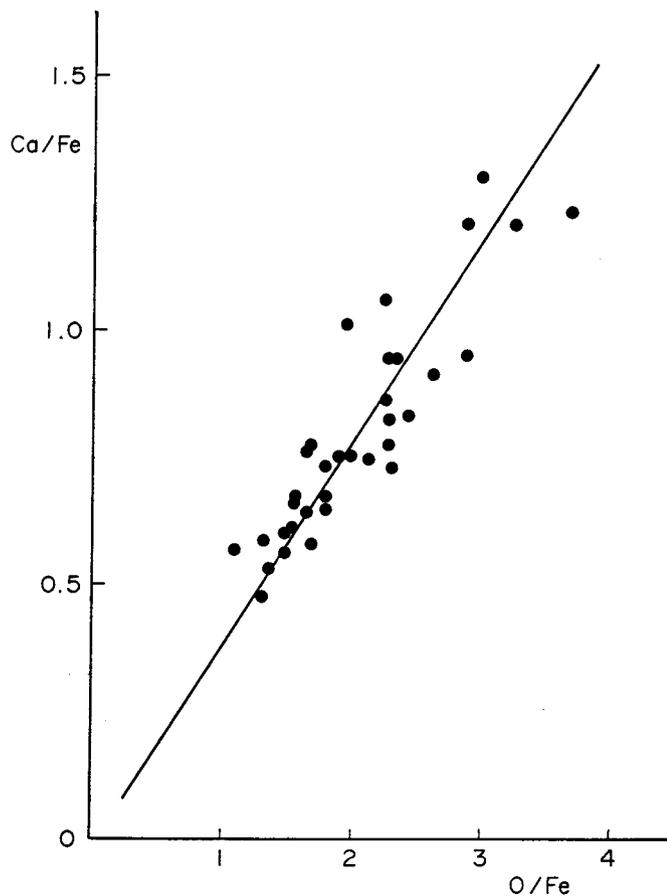


**Fig. 5.** The intensities of Al peaks are plotted against those of O peaks of a reduced triply promoted iron catalyst.

figures strongly suggest that the state of calcium and aluminium on the catalyst surfaces is in the form of their oxides.

The sum of concentration of nitrogen and sulfur was plotted against that of oxygen, which is given in Fig. 7. It is demonstrated in the figure that the surface oxygen, or promoter oxides, such as alumina, inhibits the nitrogen chemisorption, while nitrogen is not adsorbed on the surface covered by sulfur. Alumina is generally considered as a structural promoter which prevents sintering to keep large surface area although it decreases the specific catalytic activity. Such decrease in the specific activity is well exhibited in Fig. 7.

The distribution of each of the components in the surface of multi-component catalyst is not only different from that in the bulk, but also not uniform over the surface, which is closely associated with that of active points in the surface. It is, therefore, very important to study the activity or nitrogen adsorption at each point in the surface in connection with their

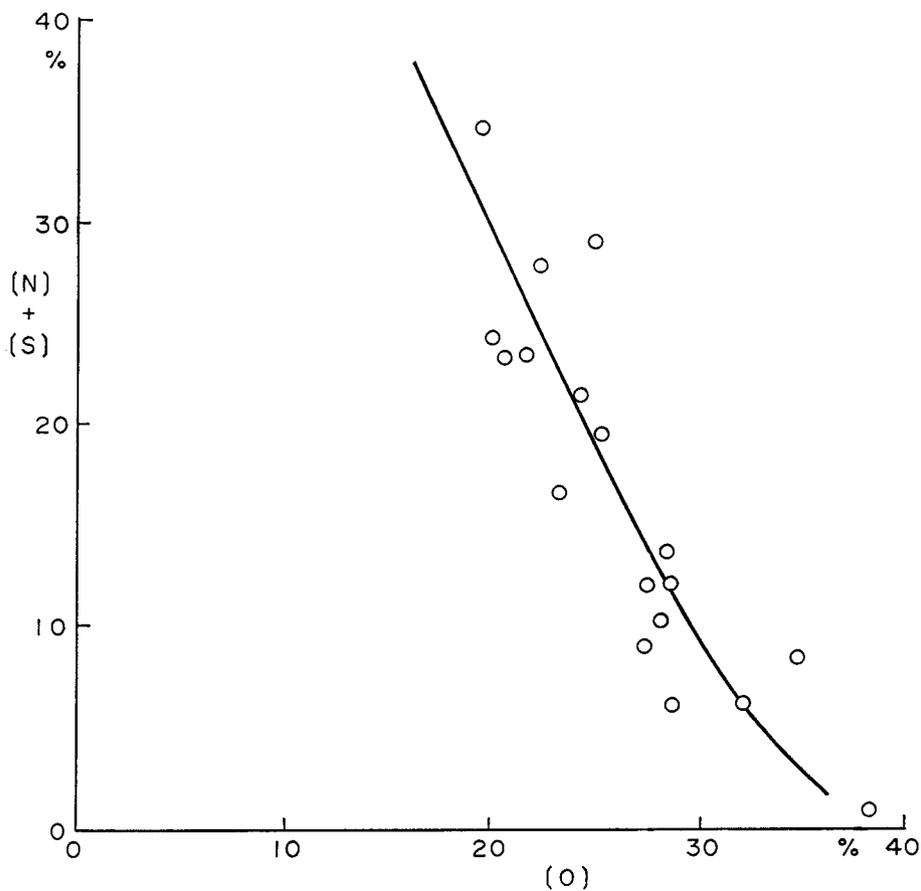
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**Fig. 6.** The intensities of Ca peaks are plotted against those of O peaks of reduced triply promoted iron catalyst.

composition to elucidate the nature of active points and the role of each component in heterogeneous catalysis. In this sense, the electron microprobe Auger technique will become a powerful tool for the study of heterogeneous catalysis.

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**Fig. 7.** The sums of surface concentration (in atomic percentage) of nitrogen and sulfur are plotted against that of oxygen on a doubly promoted iron catalyst.

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