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Poisoning of iron catalyst by sulfur

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Abstract

The influence of sulfur on the activity of iron catalyst in the reactions of ammonia synthesis, ammonia decomposition and iron carburization in methane has been studied. The activity of iron catalyst in all reactions under study drops with increasing concentration of sulfur. The normalized activity of iron catalyst poisoned with sulfur depends on temperature: the higher the process temperature the higher normalized activity. The apparent activation energy of all considered processes increases with sulfur content in the catalyst. Simple site-blocking mechanism of poisoning cannot be applied, therefore, a complex mechanism of poisoning is proposed. It comprises a superposition of the site-blocking, the formation of sulfur–alkali metal compounds and a change of the number of active sites driven by temperature.

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1. Introduction

Sulfur adsorbs very strongly on metals [1] and modifies or even prevents the further adsorption of other molecules [2]. Its presence on a metal surface usually effects substantial loss of activity in many reactions. In some reaction systems, it can be desirable, but in most cases it is not. Iron plays important role as a catalyst. It is commonly used in the process of ammonia synthesis [3] and frequently applied to the Fischer–Tropsch synthesis [4]. Recently, nanometric iron is used as a catalyst in the process of carbon nanotubes formation [5]. The literature on the interactions of various sulfur compounds on iron surface is quite abundant [6–29]. However, the influence of sulfur compounds on the reactions taking place on real substrates made of iron has received relatively little attention. It has been mainly focused on two fields: ammonia synthesis [30–35] and corrosion reactions [36–40].

Depending on the composition of iron catalyst for ammonia synthesis, the amount of sulfur required to its complete deactivation differs. It was reported that for singly (Al_2O_3) promoted catalyst no more than 3% of sulfur coverage effected rapid drop of activity to zero, however, doubly promoted catalyst, containing Al_2O_3 and K_2O, maintained 20% activity at sulfur coverage exceeding 30% [33]. Only about 0.2 mg S/m^2 of iron surface was sufficient for complete deactivation of catalyst [32] and it was shown that catalyst containing the addition of potassium compounds was significantly more resistant to sulfur poisoning [30,34]. The latter effect was attributed to gettering effect of the alkali promoter and formation of K_2S or KHS compounds. If the concentration of sulfur was 0.4–0.5 mg/m^2 of iron surface formation of bulk FeS was observed [32]. Detrimental effect of sulfur was also observed for ammonia decomposition on iron [41]. The poisoning effect of sulfur on catalytic activity of iron surface was generally explained by a simple site-blocking of active sites [2].

The reactions of carbon-bearing gases with iron surface is also influenced by the presence of sulfur. This effect was intensely studied for the corrosion processes of mechanical parts. During a high-temperature carburization of iron and its alloys the formation of graphite deposition on iron was significantly retarded in the presence of H_2S [28,36,39,40]. Correspondingly to the sulfur influence on catalytic activity of iron, Grabke et al. have attributed the sulfur effect to the site-blocking mechanism [37,38].

As described before the studies on the sulfur effect on the reactions taking place on iron surface were carried out on substrates of different structure (bulk and porous materials). Therefore, the direct comparison of obtained results for all of these processes is not easy to perform. The main goal of the present paper is to study the effect of sulfur on several

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processes, namely ammonia synthesis and its decomposition on iron as well as carburization of iron, on identical substrate under similar conditions.

2. Experimental

2.1. Substrate

As a substrate an industrial iron catalyst for ammonia synthesis was chosen. In its active, reduced and unpoisoned form, it contained, apart from iron, 3.3 wt.% Al_2O_3, 2.8 wt.% CaO and 0.65 wt.% K_2O. The catalyst was in form of small grains in fraction from 1 to 1.2 mm. The size of grains was chosen so as to perform all catalytic reactions in the kinetic region of reaction, so as there was no influence of external or internal diffusion effects. The specific surface area of a fresh sample was measured by BET method and amounted to 13 m^2/g. The average size of crystallites measured by broadening of XRD peak was 19 nm.

2.2. Poisoning by sulfur

Sulfur was introduced into the fresh iron catalyst by impregnation from a dilute water solution of ammonium sulfate. The grains of iron catalyst were immersed in the solution of a given concentration of $(NH_4)_2SO_4$ and then solvent was evaporated under vacuum at 70 °C, while the sample was continuously stirred. Afterwards the catalysts' samples were dried for 24 h at 150 °C. The samples of four different sulfur concentration in the catalyst were obtained in that way. The sulfur concentration was evaluated by AES-ICP method and amounted to: 350, 920, 1650 and 2500 ppm. The sulfur concentration was also analyzed in the used samples after ammonia synthesis. The obtained concentrations were 380, 860, 1580 and 2400 ppm, respectively. The difference between the sulfur concentrations in fresh and used catalysts lays within the experimental error. It shows that during the processes under study the loss of sulfur from the catalysts' bulk is negligible.

2.3. Ammonia synthesis

The activity of iron catalysts in the ammonia synthesis reaction was measured with use of a high-pressure installation. Two gram of each poisoned sample as well as a sample of the fresh catalyst was placed in a six-channel steel reactor. Prior to activity measurements all samples were reduced under the flow of hydrogen-nitrogen atmosphere. The process was carried out polythermally. Temperature was raised from ambient up to 525 °C for 24 h. The samples were then conditioned at 525 °C for 2 h. The activity tests were performed under the pressure of 10 MPa. Activity of each sample in the reaction of ammonia synthesis was measured at 400, 450 and 500 °C. The space velocity of the gas mixture was maintained at 25,000 h^{-1}. The concentration of ammonia in each channel of the reactor was measured on the basis of IR absorption.

As a measure of the activity a reaction rate constant k_2 from Tiomkin-Pyzhev equation shown below was taken.

$$r = k_2(0.75)^{1.5}P^{-0.5}\frac{(1-Z)^{2.5}}{Z}\left[\frac{(Z^{eq})^2}{(1-Z^{eq})^4} - \frac{Z^2}{(1-Z)^4}\right]$$

where P is the synthesis pressure, Z dimensionless current concentration of ammonia, and Z^{eq} is the dimensionless equilibrium concentration of ammonia.

2.4. Ammonia decomposition

Experiments were carried out in a tubular glass reactor with an electric furnace. In each experiment 0.5 g of iron catalyst was placed in a platinum basket. Prior to the ammonia decomposition experiments the catalyst was reduced under the flow of pure hydrogen (200 sccm). The process was carried out polythermally. Temperature was raised from ambient up to 525 °C. The samples were conditioned at 525 °C for 2 h. Next the hydrogen atmosphere was exchanged with pure ammonia (99.997%, flow 200 sccm) and ammonia decomposition experiments were performed at 450, 475, 500 and 525 °C. The concentration of ammonia in the gas mixture leaving the reactor was measured on the basis of IR absorption.

2.5. Carburization of iron

Experiments were carried out in a tubular glass reactor with thermogravimetric measurement being a part of an electronic spring thermobalance. In each experiment, 0.5 g of iron catalyst was placed in a platinum basket. Prior to the experiments the catalyst was reduced under the flow of pure hydrogen (200 sccm). The process was carried out polythermally. Temperature was raised from ambient up to 700 °C. The samples were conditioned at 700 °C for 2 h. Next the hydrogen atmosphere was exchange with pure methane (99.99%, flow 200 sccm) and the carburization of iron was performed at 625, 650, 675 and 700 °C. The mass gain of the sample during the process was recorded.

3. Results and discussion

The iron catalysts poisoned with sulfur are significantly less active in ammonia synthesis reaction than unpoisoned one. This is illustrated in Fig. 1 showing that normalized activity (the rate constant of the poisoned catalyst normalized with respect to that for the fresh catalyst) for the catalysts drops rapidly with increasing sulfur concentration, what is in line with previous observations [33]. At 400 °C, the catalysts containing 1650 ppm and more of sulfur are almost completely inactive, whereas, at 500 °C they still maintain about 20% activity. In the whole range of sulfur concentration in the catalyst the higher the process temperature the higher normalized activity is.

In the processes of ammonia decomposition and iron carburization, the influence of sulfur on the activity is similar. In Fig. 2 it is shown that with increasing sulfur concentration the normalized activity of the catalyst in the ammonia

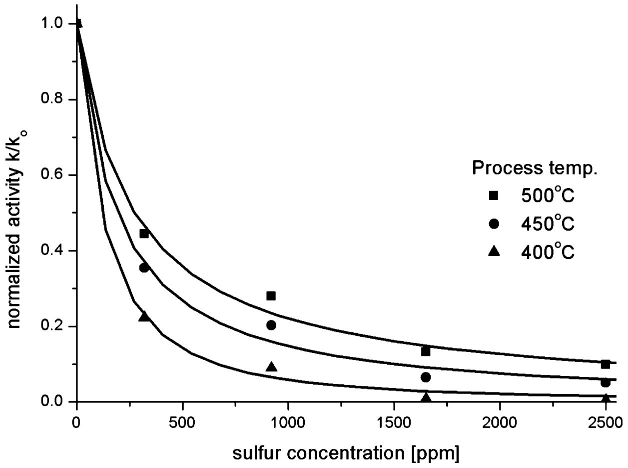

Fig. 1. Sulfur effect on the normalized activity of iron catalyst in the reaction of ammonia synthesis (10 MPa, space velocity 25,000 h^{-1}).

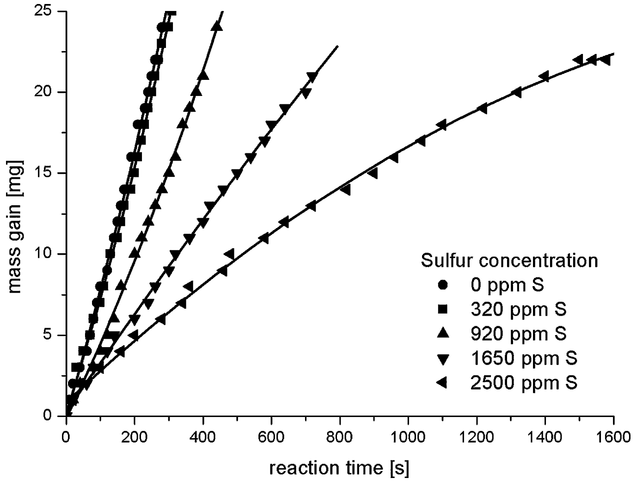

Fig. 3. The mass gain of iron catalyst poisoned with different sulfur doses during carburization in methane atmosphere at 675 °C (atmospheric pressure, ammonia flow 200 sccm).

decomposition process decreases substantially. However, the catalyst seems to be more resistant to the sulfur poisoning than it is observed in the ammonia synthesis process. At the highest content of sulfur the catalyst maintains about 40% activity in comparison to the 20% activity observed in the ammonia synthesis. The process of iron carburization is also influenced by sulfur (Fig. 3). At the initial stage of the reaction between iron catalyst and methane the only solid product is iron carbide, Fe_3C, what is confirmed by the XRD analysis. At this stage, the observed mass gain of the samples is approximately linear. Assuming this linear dependence the reaction rate constants for iron carburization performed with the iron catalyst containing different amount of sulfur were calculated and they are displayed as normalized activity in Fig. 4. Correspondingly to previously described reactions the normalized activity decreases with increasing concentration of sulfur and, for a given sulfur contents, increases with increasing temperature.

Basing on the calculated rate constants of the reactions under study the apparent activation energies of all processes were evaluated for each sulfur concentration and the results are shown in Fig. 5. The apparent activation energy for fresh catalyst in ammonia synthesis is 176 kJ/mol. Typical value for the apparent activation energy in this process ranges from 170 to 180 kJ/mol [42]. With increasing concentration of sulfur it increases to 258 kJ/mol. For iron carburization in methane the respective values are 176 and 238 kJ/mol. The apparent activation energy for ammonia decomposition changes from 38 to 70 kJ/mol.

The results obtained for all reactions under study have several common features. Activity in all processes drops with increasing content of sulfur and this drop is of a non-linear character. The influence of the first doses of sulfur on activity of iron catalyst is much more prominent in comparison to the effect of the subsequent doses. It is especially evident for ammonia synthesis and ammonia decomposition. Moreover, in all processes the temperature dependence of normalized activity is also observed, i.e. the higher is process temperature the higher normalized activity for a given sulfur concentration

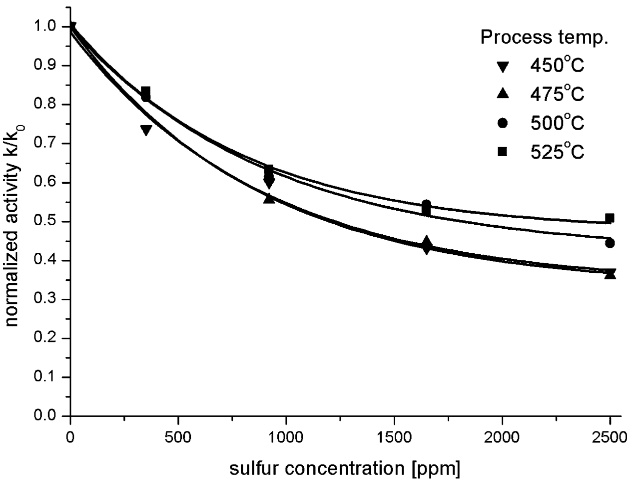

Fig. 2. Sulfur effect on the normalized activity of iron catalyst in the reaction of ammonia decomposition (atmospheric pressure, ammonia flow 200 sccm).

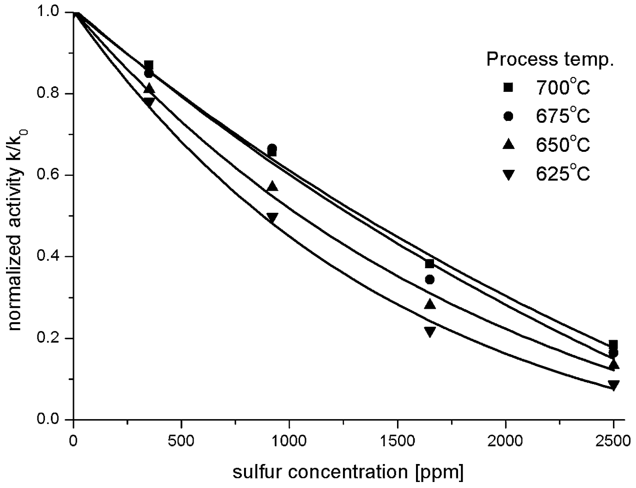

Fig. 4. Sulfur effect on the normalized activity of iron catalyst in the reaction of iron carburization in methane (atmospheric pressure, ammonia flow 200 sccm).

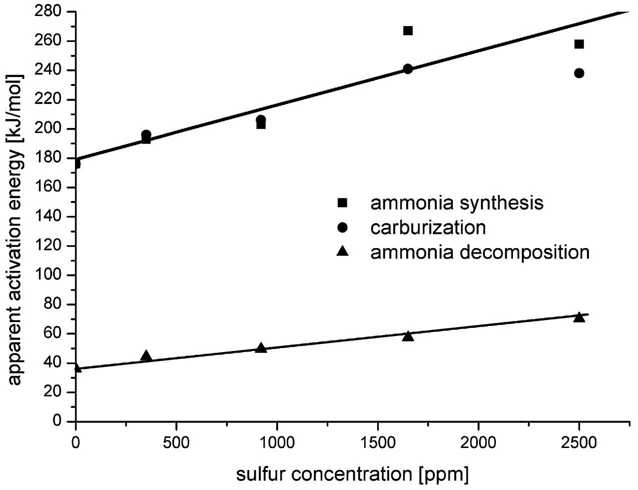

Fig. 5. The apparent activation energy of ammonia synthesis, ammonia decomposition and iron carburization in methane as a function of sulfur concentration in iron catalyst.

in the catalyst is observed. This dependence is also reflected in the change of the apparent activation energy of all processes with raising poisoning degree.

Bartholomew et al. [2] summarized the reports on the effect of sulfur on catalytic activity of several catalytic systems. Among others the catalysts for steam reforming, CO hydrogenation and ammonia synthesis were analyzed. The general conclusion was that the poisoning involved primarily a geometric blocking of active sites by adsorbed sulfur. This statement was based on several common features of analyzed processes. For all of these systems the activity dropped with increasing sulfur dosage and it was on non-linear character what corresponds with the results shown in the present paper. In several cases it was possible to linearize the normalized activity expressing it as a function of non-poisoned iron surface. Usually a function $(1 - \theta/\theta_S)$ [43] or its quadratic form $(1 - \theta/\theta_S)^2$ [7,31] were used, where θ and θ_S are sulfur coverage and saturation sulfur coverage, respectively. This observation implied a simple geometric effect of sulfur on activity. The second important finding was independence of the apparent activation energy on the poisoning degree. Therefore, it was concluded that the electronic effects of sulfur on the iron surface are negligible. In general, a simple site-blocking mechanism of sulfur poisoning was proposed.

In the present paper, this approach failed. Linearization of the normalized activity curves was unsuccessful and the dependence of the apparent activation energy on sulfur content was observed for all reactions under study.

The explanation of these discrepancies probably lies in the complexity of the studied systems. The data analyzed by Bartholomew et al. [2] were collected on clean metal surfaces and simple, singly promoted iron catalysts [7,31]. However, the reports concerning the ammonia synthesis on doubly promoted iron catalyst are not so unambiguous [33].

In the present paper, the much more complex system, the triply promoted iron catalyst for ammonia synthesis is considered. The active surface of iron catalyst is a composite system. The main constituent is iron and it has been claimed that Fe(1 1 1) surface is the dominant surface plane [44]. However, under real conditions other iron faces containing both steps and terraces are thought to be present. It is well-known that the adsorption sites on the step edges are more active than those on terraces. Sulfur deactivates the steps as it was recently shown for nickel (1 1 1) surface [45]. If the influence of the adsorption sites at step edges is significant for the total activity of the catalyst the deactivation of those few sites by relatively small amount of poison can lead to the substantial loss of catalyst's activity. Recently, Dahl et al. [46] shown for the industrial iron catalyst that only about 5% of the total number of adsorption sites on the catalyst are capable to bind nitrogen. The rest of adsorption sites are filled by diffusion. Taking these findings into account one may suggest that the first doses of poison deactivates sites which are important for the dissociative adsorption of nitrogen. This process leads to the considerable loss in activity as observed in Figs. 1–4. Further doses of sulfur deactivate other sites on iron surface but their influence on the activity is not so prominent. In that way, the simple site-blocking mechanism valid for clean and plain metal surfaces is not applicable to this complex system as iron catalyst for ammonia synthesis is.

However, the reasoning presented above does not cover the full complexity of iron catalyst. Sulfur can undergo many different processes from which an adsorption on metal surface is only one. The modern models of active surface of iron catalyst for ammonia synthesis [47–51] suggest that this surface is to a large extent covered with a complex structure made of oxygen and alkali promoter atoms. Considering the existence of free iron surface regions with the patches of promoters on it the formation of sulfur islands is also possible. The mechanism of island growth was found to be valid for the adsorption of sulfur on clean iron surface [24].

Moreover, sulfur was supposed to react with potassium compounds present in the iron catalyst and form K_2S or KHS compounds [30,32,34]. In that case, an electronic influence of adsorbed sulfur on the activity of the surface cannot be easily neglected.

None of mentioned effects cannot be ruled out, however, there is also a lack of direct evidences for each of them.

The important effect observed in the present study is an increase of relative activity of catalyst with the increasing temperature. This process can happen either when some of active sites blocked by sulfur are freed or in case of the formation of additional free active sites. There was no substantial loss of sulfur in the used catalysts, therefore, the removal of sulfur from catalyst with the increasing temperature can be ruled out from the considerations. However, the reaction between adsorbed sulfur and alkali promoter followed by a migration of formed compound from the active surface can be taken into account. If one considers a dose of sulfur added to the catalyst it must be divided in two parts: one is adsorbed on the iron surface the other reacts with alkali atoms. The formation energy of alkali metal–sulfur compounds is smaller than adsorption energy of sulfur on iron surface [41] and at first the adsorption on free sites dominates. However, with increasing concentration of sulfur the number of free adsorption sites will drop and the driving force to form a compound with alkali metal will probably increase.

The evolution of an active surface of fused iron catalyst with the temperature was already supposed in literature [52]. This concept assumes that the surface of iron catalyst is in thermodynamic equilibrium and the number of active sites can slightly change with the temperature due to a reconstruction of the catalyst's surface. The driving force of this process is a difference between the surface energy of iron and the formation energy of the oxygen–alkali metal compounds [52].

It can be supposed that the effects observed for iron catalyst poisoned by sulfur are superposition of two main processes: a simple, geometric effects of site-blocking by sulfur atoms and an evolution of the number of active sites with the temperature of process. The former was proven to be valid for clean iron surface and it would not be discussed further in the text. To give reason for the latter a reasoning is presented below.

As it was supposed above if small dose of sulfur is added to the fresh catalyst sulfur atoms should predominantly adsorb on free adsorption sites. Therefore the region of small sulfur concentration reflects this component of sulfur effects which can be attributed to the site-blocking only. To check this assumption a tangent to the curve of normalized activity in a point of zero sulfur concentration was drawn in Fig. 6. The tangent line was as long to intersect with the axis of abscissa. The intersection point determines the concentration of sulfur required for complete deactivation of catalyst in case when only site-blocking would affect the process. From the concentration of sulfur found in the intersection point the normalized number of free sites in catalyst can be calculated: $N_f = c_S N_A / S$, where c_S, N_A and S are sulfur concentration, Avogadro number and specific surface area of catalyst, respectively. This reasoning and calculation was applied to all processes and catalyst under study. The results are shown as a function $\ln(N_f) = f(1/T)$ in Fig. 7.

For all reaction the linear dependence of $\ln(N_f)$ on reciprocal temperature is observed. Moreover, the slope of all lines are virtually identical. The processes of ammonia decomposition and iron carburizing with methane can be even drawn with use of one straight line. The results suggest that there is a common process, driven by temperature, which influences the surface of iron catalyst to the same extent independently to the atmosphere the catalyst is used in. The normalized number of free sites, N_f, increases with temperature for each reaction and this can explain the effects observed in Figs. 1–4. Because the magnitude of both the specific surface area and the active surface for a given catalyst cannot be measured under the reaction conditions there is no direct evidences corroborating the presented hypothesis. However, it seems justified in the light of the presented results.

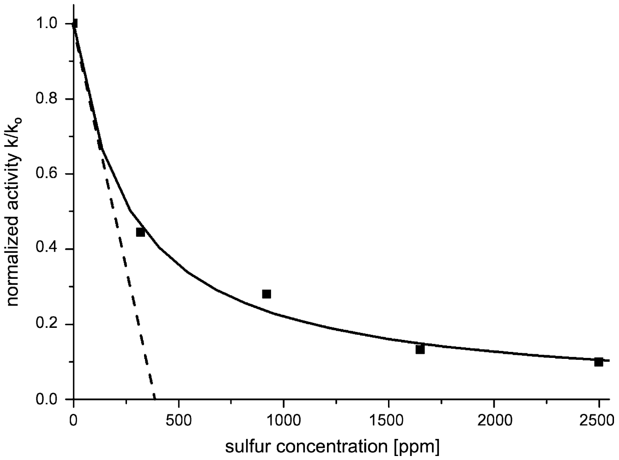

Fig. 6. Normalized activity of iron catalyst in the ammonia synthesis process at 500 °C (10 MPa, space velocity 25,000 h^{-1}). Dashed line is a tangent of normalized curve at zero concentration of sulfur.

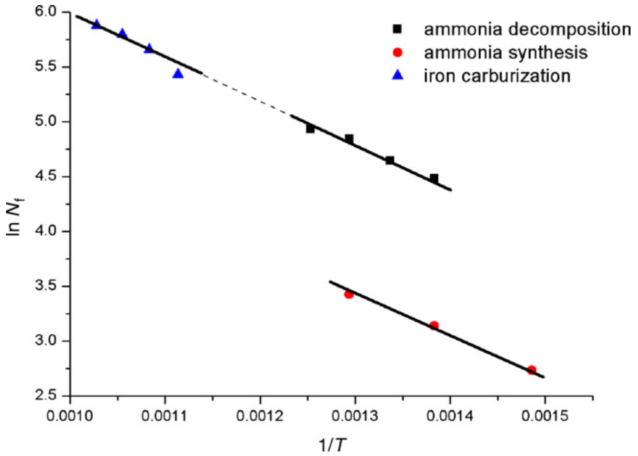

Fig. 7. Logarithm of normalized number of active sites vs. reciprocal temperature.

4. Conclusions

The effect of sulfur on the activity of iron catalyst used in ammonia synthesis, ammonia decomposition and iron carburizing under methane atmosphere is a complex phenomenon. Several different processes and mechanisms can be put forward to elucidate it, among others: site-blocking of active sites by sulfur atoms, the formation of stable compounds between sulfur and alkali promoters and the evolution of a number of active sites on the surface of iron catalyst with the temperature. The lack of direct evidences for the two latter processes should be an inspiration for a further studies.

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