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Double-Layer Model of the Fused Iron Catalyst for Ammonia Synthesis[†]

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A new model of the surface of a fused iron catalyst for ammonia synthesis is proposed. It is assumed that the iron surface is covered with a double layer due to wetting by promoter oxides. The first sublayer in the direct vicinity of the iron atoms is filled with oxygen atoms and the free adsorption sites are present in this sublayer. The second sublayer located over the first one is filled with promoter atoms. The number of oxygen atoms and free adsorption sites is determined by the nature of the promoter. Every atom of alkali metal needs one oxygen atom to be stable on the iron surface under ammonia synthesis conditions; one atom of alkali earth element needs two oxygen atoms; one atom of aluminum needs three. The number of the free adsorption sites is directly related to the number of oxygen atoms on the surface. The more oxygen atoms on the iron surface, the less free adsorption sites are available for dinitrogen adsorption. The surface area of the iron catalyst is also dependent on the number of oxygen atoms on the surface. Therefore, elements such as Ca and Al, which need a high concentration of oxygen on the surface, lead to the formation of the catalyst exhibiting the highest surface area. Between the surface, the iron bulk, and the spacers located between the iron crystallites the thermodynamic equilibrium is maintained. On the basis of this model an interpretation of some properties of the iron catalyst is presented.

Introduction

Interest in the structure of a fused iron catalyst and its influence on the ammonia synthesis reaction began in the early years of the 20th century when Haber, Bosch, and Mittasch introduced this catalyst to industrial practice. Many studies concerning this subject have been performed since then. During the late 70s new spectroscopic methods were introduced to the studies of the iron catalyst, and they enabled atomic level studies on well-defined single-crystal surfaces. This new approach together with developed methods of characterization of the industrial catalyst has led to better understanding of the ammonia synthesis mechanism. The 90s have brought several monographs on the ammonia synthesis.^{1–3} Despite numerous studies of the kinetics and mechanism of the ammonia synthesis reaction, some results and conclusions are still incomplete and controversial.⁴

The industrial iron catalyst for ammonia synthesis consists of reduced iron and a few additives, mostly Al₂O₃, CaO, and K₂O. The oxides Al₂O₃ and CaO, which are believed to increase the catalytic activity primarily by increasing the total area of the catalyst, are referred to as structural promoters. Some other oxides, especially K₂O, which influence the activity by increasing the reaction rate per area, are referred to as chemical or electronic promoters. The intensive studies performed during the last 30 years have revealed the complex composition of

the iron catalyst, with regard to its morphology and the surface structure. The influence of the structure of iron surfaces on the limiting stage of ammonia synthesis, namely dinitrogen adsorption, was found in the late 70s.^{5,6} This structure sensitivity was also found for the ammonia synthesis reaction.^{7,8} These studies revealed that the iron faces, Fe(111) and Fe(211), are the most active and that they are followed in reactivity by Fe(100), Fe(210), and Fe(110). Many studies were devoted to the role of potassium. Ertl et al. reported the disappearance of differences in the rate of dinitrogen dissociative adsorption on different iron surfaces after potassium adsorption.⁹ Because the presence of potassium on the iron surface increases the rate of dinitrogen adsorption, leading to a higher rate of the ammonia synthesis, it is very important to know the mechanism of its operation. The most important question is the chemical form of potassium on the iron surface. It was found that potassium in the metallic form cannot be present on the catalyst surface under ammonia synthesis conditions.¹⁰ AES studies show that potassium desorbs from the iron surface at about 480 K.¹¹ According to the TPD studies, potassium is present on different iron surfaces (Fe(111), Fe(110), Fe(100),^{12,13} and Fe(poly)¹⁴) even at the temperature 900 K with the presence of oxygen atoms which increase the thermal stability of potassium.^{11,14} On the basis of these

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results, an undefined structure (K + O) has been proposed as an active surface of the iron catalyst.^{14,15}

To specify the structure of the active surface of the iron catalyst, a simple model has been proposed.¹¹ Potassium atoms are adsorbed on the iron surface, and the free sites for adsorption of nonmetals are located under the layer of potassium atoms. These sites are partly occupied by the oxygen atoms which stabilize the potassium atoms on the iron surface under the ammonia synthesis conditions. The presence of hydrogen is not considered because of the small size of its atoms and because potassium does not influence the rate of its adsorption.¹⁶ It is assumed that from the geometric point of view there is enough space for the hydrogen atoms. The nitrogen adsorption followed by the ammonia synthesis reaction may take place in a layer located under potassium atoms.

Besides the models presented above at least two other models of the iron catalyst surface can be found in the literature.^{17,18} The first one suggests that the presence of alumina on the iron surface leads to the surface restructuring. Alumina forms an iron aluminate on the surface. After exposure to the reaction mixture, iron grows on iron aluminate with a (111) or (211) orientation, which, as mentioned before, are the most active faces of iron. The second one proposes that promoters are present in the surface islands less than 1 nm in thickness and approximately 2 nm in diameter and that between them there is pure iron. None of the mentioned models explain every experimental observation. We believe there still is a need for a new proposal in this field.

Model

A new view on the results published in the literature inclined us to build a new model of the surface of the iron catalyst. Its basis is the model presented above.¹¹ A few assumptions have been made to construct this model.

Assumption 1. The previously described model can be applied not only for potassium but also for other promoters. Promoter and nonmetal atoms are located in two separate layers. The layer in the direct vicinity of iron atoms is "reserved" for oxygen and other nonmetal atoms. The free sites for nitrogen adsorption are located in this layer. The promoter atoms are located "on top" of the oxygen atoms forming topmost layer (Figure 1a).

Assumption 2. The ratio of the number of oxygen atoms to the number of promoter atoms located on the iron surface is constant and equal to the valence of the promoter (for alkali metals, 1:1; for alkali earth elements, 2:1; for aluminum, 3:1). Thereby, the number of oxygen atoms on the iron surface is determined by the nature of the promoter.

These two assumptions are closely related to each other. The "on top" configuration was proposed the first time by Papageorgopoulos and Chen for cesium adsorption on Ni(100) and W(100).¹⁹ Paal et al.¹⁴ considered this configuration for potassium and oxygen adsorption on the iron surface and rejected it as inconsistent with their results. It was found that at least two oxygen atoms are necessary to stabilize one potassium atom on the iron surface. It was stated that even in this configuration there was enough space for potassium and oxygen coadsorption with K/O = 1:2 (the ionic radius of the atoms was assumed). Indeed, simple calculations confirm this statement but in

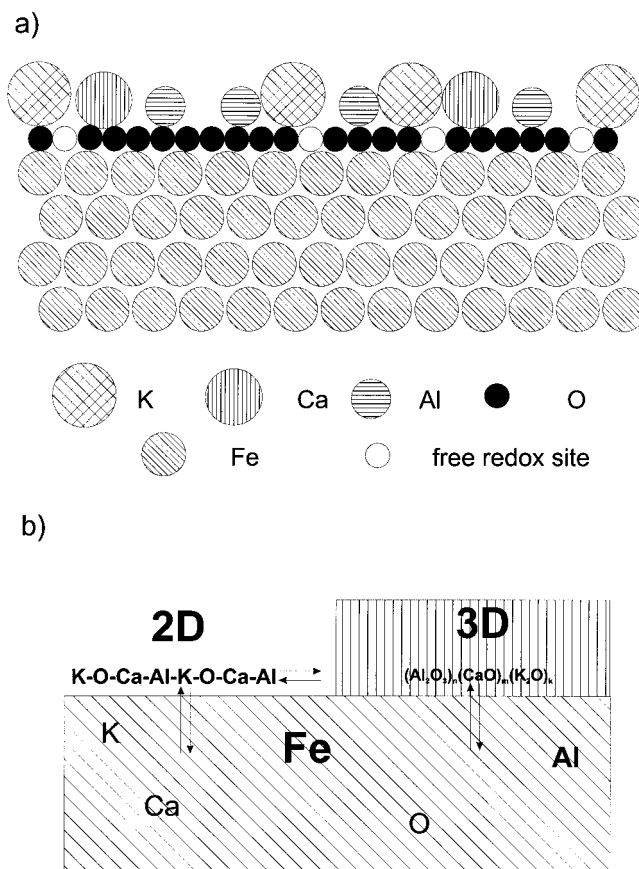


Figure 1. (a) Double-layer model of the surface of the iron catalyst. (b) Scheme of the equilibrium between the surface, the iron bulk, and the three-dimensional structures in the iron catalyst.

this case there is no free space for adsorption of other species (N₂). The final conclusion presented by Ertl¹⁵ is that the K/O ratio under ammonia synthesis conditions is 1:1. These results are confirmed by other works^{11,20} and are accepted in the present paper.

The evidences concerning the Me/O ratios for alkali earth elements and for aluminum are indirect. As mentioned before, the chemical valence is taken as a criterion. Potassium is a univalent metal, and the respective ratio is 1:1; for two-valent and three-valent elements the ratio is assumed to be 1:2 and 1:3, respectively. Some experimental results have been found to confirm this assumption. Upon heating of the iron surface contaminated with calcium, the Ca/O ratio appeared to be 1:2.²¹ Also, the studies of the coadsorption of barium and oxygen on the copper surfaces prove that the identical ratio is true for the Ba/O system both before and after heating to 800 K.²²

Assumption 3. The iron surface is "wetted" by promoter oxides. The potassium atoms can migrate on the iron surface under ammonia synthesis conditions to adsorb on the free iron atoms or cover the layer of the other promoter oxide present there before.²³ A recent paper²⁰ demonstrates that under ammonia synthesis conditions a clean iron surface which is in direct contact with the multiply promoted iron catalyst is covered with a potassium-oxygen layer. This result indicates that despite the

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Table 1

promoter	atom radius r_{at} (pm)	recalculated atom radius r_{cal} (pm)	no. of promoter atoms in monolayer		no. of coadsorbed oxygen atoms ($\times 10^{18}$ m $^{-2}$)		no. of free sites		surface area (m 2 g $^{-1}$)		no. of free sites (m 2 g $^{-1}$)		electro-negativity by Pauling	promoter content sufficient to cover monolayer (wt %)
			Fe(111)	Fe(100)	Fe(111)	Fe(100)	Fe(111)	Fe(100)	Fe(111)	Fe(100)	Fe(111)	Fe(100)		
Li	152	147	14	12	14	12	0	0	20	20	0	0	1.0	0.7
Na	186	179	9	9	9	9	5	3	12	15	60	45	0.9	0.6
K	227	219	6	6	6	6	8	6	8.5	10	68	60	0.8	0.48
Rb	248	239	5	5	5	5	9	7	7	8	63	56	0.8	0.54
Cs	267	258	4.3	4.3	4.3	4.3	9.7	7.7	6	7	59	55	0.7	0.6
Mg	160	154	14(7)	12(6)	14	12	0	0	20	20	0	0	1.2	0.93
Ca	197	190	8(7)	8	14	12	0	0	20	20	0	0	1.0	1.11
Sr	215	207	7	7	14	12	0	0	20	20	0	0	1.0	2.22
Ba	219	211	6.5	6.5	13	12	1	0	18	20	20	0	0.9	2.92
Al	143	138	16(4.5)	12(4)	14	12	0	0	20	20	0	0	1.5	0.76

presence of other promoters (Al, Ca) in the catalyst it is potassium that covers the iron surface. Even prolonged maintenance of such a sample under ammonia synthesis conditions (700 K, 10 MPa) does not change the composition of its surface.

Assumption 4. The equilibrium between the bulk, the surface, and the spacers placed between the iron crystallites is kept (Figure 1b) and the total surface area is determined by the number of oxygen atoms on that surface.

This assumption is based on many observations of the behavior of the industrial catalysts. The iron catalyst for ammonia synthesis is very stable and possesses a long catalyst life. Despite of the high porosity and severe work conditions (high temperature and high pressure), the structure of this catalyst remains almost unchanged for years. A slow sintering observed during catalyst use seems to be caused mainly by a local overheating. A system which is far from equilibrium would tend to reach this state as fast as possible, which is not observed in the case of the iron catalyst for ammonia synthesis. However, a change of the chemical composition of the catalyst, for example, potassium addition to the Al-promoted catalyst, causes an immediate change of its surface area.²⁴

The second part of assumption 4 should be explained thoroughly. The clean iron surface exhibits a tendency to minimize an excess of the surface energy by reduction of the surface area. It is assumed in the model that the surface is covered by an oxygen layer (there are promoters on top). In this case the surface energy is compensated by Fe–O bonds. The greater the oxygen concentration, the higher the amount of Fe–O bonds and the greater the surface area should be. The catalyst containing the elements which need more oxygen atoms (Ca, Al) to be stable on the iron surface at a high temperature exhibits the highest BET area, reaching about 20 m 2 /g.²⁵ The lowest excess of the surface energy of the iron surface covered with oxygen is reached for the oxygen monolayer. For this reason the value of 20 m 2 /g is taken, as in the case with a monolayer of oxygen on the iron surface, and is used in the subsequent calculations.

Considering the proposed assumptions, we can calculate the quantitative relationships between the atoms of iron, oxygen, and promoters on the surface of a model catalyst. Therefore, knowledge of the number of adsorbed oxygen atoms on the iron surface is necessary. The iron faces Fe(100) and Fe(111) are considered in the subsequent calculations. The surface structure formed by oxygen atoms on the Fe(100) face is described as Fe(100)p(1 \times 1)–O, and the number of oxygen atoms in the monolayer is 12×10^{18} m $^{-2}$.^{26,27} For the Fe(111) surface an appropriate reconstruction is Fe(111)(2 $\sqrt{3} \times 2\sqrt{3}$)R30°–O, and the number of oxygen atoms in the monolayer is 14×10^{18}

m $^{-2}$.²⁸ During studies of coadsorption of different nonmetals on the iron surface, the equation $O_S + O_{N_2} + O_{C_2} + O_{O_2} = 1$ was derived. Taking into account this equation and reconstruction structures the numbers 14×10^{18} and 12×10^{18} m $^{-2}$ are considered as the maximal numbers of free adsorption sites on the Fe(111) and Fe(100) surfaces, respectively.²⁹

The number of potassium atoms capable of being adsorbed on the iron surface should also be known. On the Fe(111) surface precovered with oxygen ($\Theta_O = 1$) the number of potassium atoms is about 6×10^{18} m $^{-2}$.¹¹ In this case the potassium atoms can be considered as close packed. With this assumption the radius of the potassium atoms is calculated as 219 pm, which is a value much greater than the radius of potassium ions (138 pm; coordination number 6) and slightly less than the radius of potassium atoms (227 pm) but very close to the covalent radius of potassium. The ratio of these radii (219/227) is taken as a reflection of the interactions between the potassium and oxygen atoms and is used for the subsequent calculation for other promoters. Results of these calculations with the assumption that the interactions between the promoter atoms and the oxygen atoms are similar to the interactions between potassium and oxygen are presented in Table 1. Considering an appropriate Me/O ratio for each group of elements, the number of oxygen atoms in the “nonmetal” layer is calculated. For some alkali earth elements as well as for aluminum the calculated number of oxygen atoms is greater than 14×10^{18} or 12×10^{18} atoms/m 2 . In this case it is supposed that the “nonmetal” layer is fully occupied by oxygen atoms but that the number of promoter atoms located “on top” is limited by the number of oxygen atoms and assumption 2. The number of free adsorption sites in the lower “nonmetal” layer is taken as the difference between the maximal number of adsorption sites on the Fe(111) or Fe(100) faces (14×10^{18} or 12×10^{18} , respectively) and the number of oxygen atoms needed on that surface. The total surface area of the model catalyst promoted by different elements and the amount of promoter oxides required to cover a monolayer of iron are also calculated. The electronegativity of each element is also included in Table

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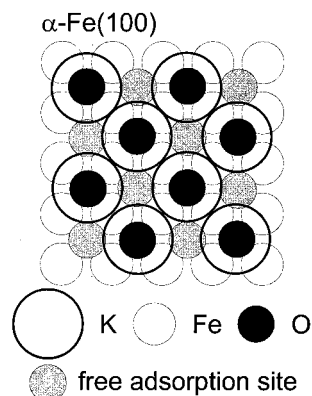


Figure 2. Top view on the Fe(100) surface covered with potassium and oxygen as proposed in the model.

1. According to the data presented above, the structure of the model catalyst and certain of its properties are estimated and compared with experiments.

Comparison of the Model and the Real Catalyst

Most of the literature concerning the influence of the promoters on the properties of the iron catalyst is focused on the role of potassium, aluminum, and calcium. Therefore, the comparison between the model catalyst and the industrial catalysts is made mainly for the former promoted with these three elements, though the model enables the interpretation of the properties of catalysts promoted with other elements. The model catalyst emerging from the aforementioned assumptions is as follows:

The surface of the catalyst is fully and homogeneously covered with a potassium–oxygen layer. Due to the assumed K/O ratio being 1:1 and regarding the location of potassium atoms on the outer layer, no other adsorption sites on the iron surface are occupied (see Table 1). According to this model, the oxygen atoms occupy from 50 to 57% of the adsorption sites on the iron surface, but since they are located under the potassium atoms, the free adsorption sites exist and are exposed to vacuum (Figure 2). Nitrogen molecules can find their way to these sites between potassium atoms.

The presented image has a lot in common with the real catalysts. TPD,³⁰ SEM/EDX, and EXAFS³¹ studies of the multiply promoted industrial catalysts show that their surfaces are completely covered with a K + O layer. The other studies carried out by means of electron spectroscopy indicate that the concentration of iron atoms on the catalyst surface is in the range 4–15%.^{32–34} Former studies which exploit the methods with a lower surface resolution give a similar view as the model. The latter methods have better surface resolution, but it is difficult to distinguish a signal originating from the surface atoms and a signal coming from atoms located underneath.

According to the model, about 50–60% of the adsorption sites are occupied by oxygen atoms. This means that there are 40–50% of the free adsorption sites which may be occupied by adsorbing nitrogen and where the ammonia synthesis reaction might take place. Therefore, this number refers to the active surface of the catalyst. This property of the catalyst is usually examined by CO

physisorption, and different values may be found in the literature,² but 40% is widely accepted to be an appropriate value.³⁵ The model is consistent with these observations. One may argue that about 60% of the iron surface might be covered with an undefined layer consisting of several elements (K, Al, Ca, O) and that the respective ratios (promoter to oxygen) do not need to be strictly preserved. However, the studies of Solbakken et al.³⁶ indicate that about 6×10^{18} of the oxygen atoms per square meter are located on the catalyst surface. This is exactly the same number found in the model. Also some other authors claim that about half of the surface of the iron catalyst is covered with oxygen.³⁷ Since the maximal number of free adsorption sites cannot exceed 14×10^{18} per square meter and the oxygen atoms are accompanied by promoter atoms on the surface, only two possible structures may be considered. The first is the “on top” location of promoter atoms assumed in the present model. The second one is a multilayer structure built from three-dimensional promoter oxides as patches located on the iron surface and mentioned before.¹⁸ This suggestion leads to the conclusion that a pronounced amount of the free iron surface is exposed to the vacuum, which is not observed by the spectroscopic methods.¹⁵

Some considerations presented here not only are able to display a model structure of the surface of the iron catalyst but also may be used to explain the influence of different elements on the catalyst properties. However, some questions arise: Why does the addition of aluminum increase the surface area of the catalyst? Why do potassium and other alkali metals exhibit a destructive influence on the surface area of the catalyst? Why is potassium used as the main activator even though Rb and Cs should change the electronic properties of the iron surface more pronouncedly and lead to a higher activity? If charge transfer is a driving force determining the activity of the surface, why do Na and Ba have a completely different influence on the catalyst properties even though their electronegativities are very similar?

The present model enables one to answer these questions. The presence of aluminum atoms on the iron surface is connected with the need for a high concentration of the oxygen atoms (assumption 2). The excess surface energy is lowered as a result of the many Fe–O bonds present on the surface. Alkali metals require less oxygen atoms to be stable on the iron surface. There are less Fe–O bonds, and the excess surface energy causes a decrease of the surface area. This conclusion is in line with many experimental results.³⁸ An industrial catalyst with potassium washed out after its rereduction exhibits a high porosity and surface area (20 m²/g), but it has a low activity. The model claims that a high concentration of oxygen leads to a high surface area but leaves no free adsites, which is a reason for the low activity. The addition of potassium and the subsequent reduction make a real catalyst about 10 times more active, but the surface area is reduced to 11 m²/g.³⁹ According to the model and the results presented previously,²⁰ potassium can replace aluminum atoms on the iron surface. This is due to the enthalpy of formation of the promoter–oxygen bonds (Figure 3). The higher the enthalpy, the higher the tendency to form bulk compounds (oxides) instead of a

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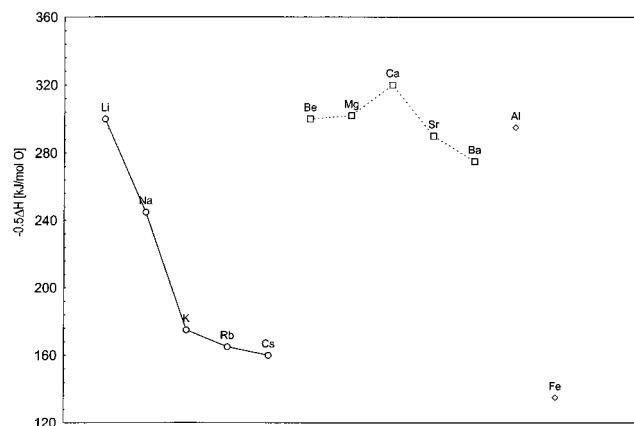


Figure 3. Strength of the bonds in promoter oxides. The total values of the enthalpies of formation of oxides are divided by the number of oxygen bonds in the respective oxide.

surface film. Therefore, potassium removes aluminum from the surface. An excess of oxygen atoms, associated previously with aluminum atoms, is removed from the surface. Less oxygen atoms leads to less Fe–O bonds a higher excess surface energy, which leads to lower surface area. Simultaneously some adsites located on the iron surface are freed and may be used for dinitrogen adsorption, resulting in a significant increase of the activity.

The exclusive use of potassium as an electronic promoter may also be explained in light of the model. Table 1 shows that the highest number of free adsorption sites per mass unit (active surface) should be found for a catalyst promoted with potassium. The surface area derived from the model for Rb- and Cs-promoted catalysts is similar to but about 20% smaller than that for a K-promoted one. Opinions in the literature on the influence of K, Rb, and Cs on the activity are split. Some authors state that the activities of the catalysts increase in the order $K < Rb < Cs$.⁴⁰ Information can also be found that fused iron catalysts promoted with Cs and Rb have about 20% lower activity than those promoted with potassium.⁴ In this light the usage of potassium seems to be more justified.

The last question concerns the difference in the influence of Na and Ba on the catalyst properties, especially its activity and the surface area. The electronegativity of these two elements is 0.9. If the action of electronic promoters relies on donation of electrons, their influence should be similar. However, these elements belong to two different

types of promoters. Sodium is considered as a promoter influencing the activity of the catalyst. On the other hand, barium is classified as a structural promoter. According to the model, the difference is obvious. Sodium enables the formation of free adsites, but barium does not. More oxygen atoms required to stabilize barium atoms lead to a higher surface area but decrease the number of free adsites.

Another feature of the catalyst which is in accordance with the experimental results is the concentration of potassium oxide required to form the active surface. The model states that 0.48 wt % K_2O is enough to cover the iron surface with a monolayer of potassium. Industrial catalysts contain usually from 0.5 to 1 wt % K_2O . An excess is required to form some bulk compounds with alumina, silicon, or calcium found in the catalyst. Because at least 10% of the potassium is permanently bound in these compounds, 0.55 wt % is considered to be a sufficient concentration. This conclusion is supported by the experimental results of Kowalczyk.³⁹ It is found that the potassium concentration in doubly promoted catalysts leads to the highest activity being in the range 0.5–0.7 wt %.

Conclusions

A new model of the fused iron catalyst for the ammonia synthesis is proposed. A double layer consisting of promoter atoms and oxygen is suggested to cover the surface. Some properties such as the surface area, the active surface area, the influence of promoter elements on the catalyst properties, and the optimal concentration of promoters in the catalyst may be estimated from the model. These properties are in good agreement with the experimental results obtained from the studies of both industrial and model catalysts. It is pointed out that promoter elements, which are conventionally divided into two groups (structural and electronic promoters), influence both the structure and the electronic properties of the surface. The structure of the surface is a result of the interaction between the iron, the promoter, and the oxygen atoms. Depending on the oxygen concentration, a porous structure without free adsorption sites or a structure with smaller surface area but with free adsorption sites may be formed. On the basis of the model, processes such as reduction, activation, and poisoning were interpreted and described elsewhere. Although the model seems to be consistent with many experimental results, more studies are still required.

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