

A study of iron catalyst for ammonia synthesis by electron spectroscopy methods*

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A concise review of former studies into iron catalyst using electron spectroscopy methods is presented. A model of iron catalyst's surface, the so-called double layer model is presented. On the basis of this model both a method of determining surface content of a real iron catalyst and a method of determining the rate of potassium surface diffusion were developed. A double layer model was used to interpret thermal stability loss of potassium atoms on iron surface subjected to sulphur compounds' exposure.

1. INTRODUCTION

The process of ammonia synthesis conducted on iron catalyst is one of the best known catalytic processes used in industrial applications. The research into the process has been carried out since its invention, i.e. for roughly one hundred years. Over that time both the basic mechanism of the reaction and the most important properties of iron catalysts were thoroughly understood [1,2]. Significant contribution into getting to know the mechanism of the reaction was due to the technique of electron spectroscopy.

Iron catalyst is a highly porous substance with specific surface area amounting to 20 m²/g consisting of small particles, 100 nm in size. Its catalytically active form consists mainly of metallic iron (approximately 90 wt%)

*This article is dedicated to Professor Tadeusz Borowiecki on the occasion of his 65th birthday

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and non-reducible oxides of such elements as aluminum, calcium, potassium and silicon, also known as promoters. Even very small changes of promoters' content in iron catalyst can lead to significant changes of its structure and its catalytic properties [3-11]. It points out to the fact that promoters play a decisive role in the process of creating a correct form of catalyst and affect catalytic processes taking place on its surface.

From the point of view of heterogeneous catalysis it is the catalyst's surface structure that is the crucial factor deciding about its catalytic activity. Bearing in mind complex character of iron catalyst a precise definition of the structure of its surface is a great challenge to researchers.

In initial studies into iron catalyst it was assumed that it consists of particles of pure iron. However, quite early on it was noticed that a significant influence of promoters, and particularly a significant influence of potassium compounds, requires that these elements be present on the active surface of the catalyst. Direct research of surface structures and particles found on iron catalyst surface composing its active surface were necessary.

2. SPECTROSCOPIC STUDIES OF IRON CATALYST

Methods of electron spectroscopy, such as Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and Low-energy electron diffraction (LEED) make it possible to determine the chemical composition and surface structure of different materials and they are widely used to investigate various materials. Unfortunately, due to high complexity of iron catalyst's structure direct and simple methods of using these techniques is either impossible or it gives averaged information, which does not really reflect the real structure of surface layer of an industrial iron catalyst.

One way of avoiding problems described above is to investigate simplified systems and then transfer obtained data to more complex systems. As early as in 1970s researchers started conducting investigations on clean surfaces of iron single crystals [12-32]. Studies on nitrogen adsorption on such surfaces demonstrated that molecular nitrogen with difficulty bonds to iron surface [21, 23, 26, 27, 31-37] and that its molecules' dissociation was considered to be the limiting step of the whole process of ammonia synthesis [38]. Studies on the behavior of potassium atoms on iron surface revealed that its atoms easily desorb from these surfaces at temperatures above 200°C. Consequently, in typical temperatures of conducting ammonia synthesis potassium should be removed from the catalyst, which was not observed [39-43]. It was established that the presence of oxygen atoms significantly increases stability of potassium atoms on iron surface [44-48] (Figure 1).

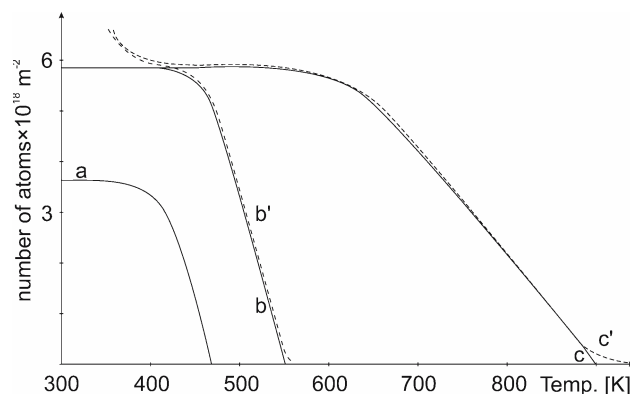


Fig. 1. Desorption of potassium and oxygen (curves marked as 'prim') from iron surface investigated using AES method: a) low oxygen content in crystal lattice of iron, no oxygen on iron surface; b) low oxygen content in crystal lattice of iron, iron surface initially covered by oxygen; c) high oxygen content in crystal lattice of iron, iron surface initially covered by oxygen [48].

The above described studies indicated that potassium atoms fixed to iron surface through oxygen bridges are necessary elements of iron catalyst surface. However, it was not quite clear what kind of space structure these atoms form on the surface and where adsorption sites are to be found, sites in which dissociative adsorption of nitrogen molecules and following on from that hydrogenation to ammonia take place [6, 9, 49-53].

Investigations of clean iron surface showed that in order to obtain the highest activity of surface the presence of C_7 adsorption sites is necessary. Such sites are found only on iron crystallographic planes (111) [5, 54-56]. However, these studies did not take into consideration presence of potassium and oxygen atoms and their influence on surface processes. In a real iron catalyst it is not expected that a significant part of iron particles will form so that C_7 adsorption sites will be found on the surface. It was suggested, though, that the presence of aluminum and potassium in catalyst can lead to reconstruction of iron surface to structures enriched with C_7 adsorption places [5, 56]. Active surface models of iron catalyst developed on the basis of the above mentioned studies suggested presence of island structures of promoters, consisting of oxygen compounds of potassium on free surface of iron [52, 53, 57, 58]. It was mainly adsorption and surface processes that were supposed to take place on the free surface of iron and potassium was supposed first of all to promote desorption of ammonia thus allowing adsorption of successive portions of molecular nitrogen.

3. MODELS OF IRON CATALYSTS' SURFACE

On the basis of the same studies, but taking into more consideration data from kinetic and structural investigations of iron catalyst, another model of surface structure of the material was put forward [59]. Iron catalyst is a structure thermally stable, which would suggest that in ammonia synthesis conditions it would be a system in a state of thermodynamic equilibrium. Therefore, it was assumed that there is thermodynamic equilibrium between two-dimensional surface phases consisting mainly of oxides of promoters found on the surface of iron particles and three-dimensional structures of catalyst's promoters and the bulk of iron particles (Figure 2). This kind of system reaches its energetic minimum when surface energy is compensated by bonds formed between oxides of promoters and surface atoms of iron.

In a reduced iron catalyst promoters occur various forms. Some of them are dissolved in the bulk of iron crystallites. Another part consisting of promoters' oxides forms structures spacing individual iron crystallites one from another. The remaining part of promoters covers iron surface. Between phases of catalyst there can be an exchange of constituents and their final composition depends on the general composition of catalyst and the temperature at which ammonia synthesis is conducted.

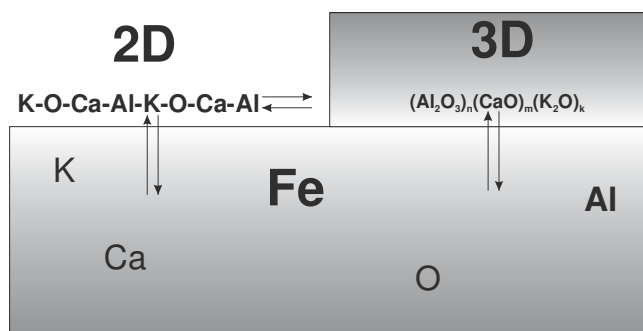


Fig. 2. Diagram of thermodynamic equilibrium between individual structures of iron catalyst and its surface [59].

On the basis of electron spectroscopic studies a double layer model of structure covering the surface of catalyst was put forward. The structure is directly responsible for the catalyst catalytic properties (Figure 3).

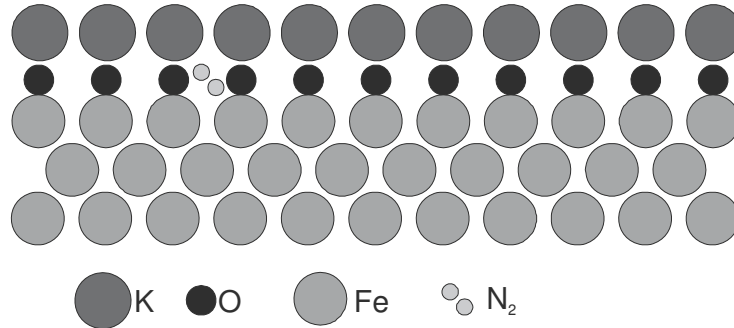


Fig. 3. Diagram of active surface of iron catalyst for ammonia synthesis promoted by potassium oxide [59].

The surface of iron crystallites is covered by a layer of promoters and oxygen in such a way that over iron atoms there is a layer containing oxygen atoms. Atoms of promoters are to be found over this very layer. The ratios between the amount of oxygen atoms and promoters atoms correspond to valence of respective elements. Consequently, the ratio of the amount of oxygen atoms to the amount of alkali metals atoms is 1:1 and the ratio of oxygen atoms to aluminum atoms is 3:1. It should also be noted that the total amount of atoms of a given promoter found on iron surface is geometrically limited by the size of its ionic radius. For example, the maximum amount of potassium atoms calculated using the method is $6 \cdot 10^{18} \text{ m}^{-2}$ which corresponds to the potassium coverage on iron surface (111), $\theta_K = 0,86$. Free adsorption sites, on which adsorption of nitrogen and hydrogen can take place and where ammonia synthesis occurs, are found between oxygen atoms above free atoms of iron.

Several important properties of the catalyst can be concluded from an analysis of the above presented model, results of investigations on industrial catalysts, model catalysts and surface structure investigations. Two kinds of adsorption sites which are to be found on the catalyst's surface can be differentiated. The first kind is found in the same layer as oxygen atoms and below promoters' atoms. Owing to this kind of placement they have a redox character. These sites are responsible for the activity of iron catalyst in ammonia synthesis. The other kind of adsorption sites can be found when iron surface is completely covered by oxygen and when aluminum or calcium are also found. In this case, no free adsorption sites are formed over iron atoms. However, particles can be adsorbed on oxygen atoms. These places can have acidic character. The number of redox adsorption sites on one unit of catalyst's surface promoted by alkaline elements, when the surface is completely wetted by these atoms, is basically due to geometrical packing of ions with given ionic radiuses and

respective relationships can be presented as the following series: Cs > Rb > K > Na. In a catalyst promoted by lithium there should be no free redox sites. Specific surface area of catalysts is a result of the number of bonds formed between iron and oxygen and it can be presented as the following sequence: Li > Na > K > Rb > Cs for alkaline elements. For other promoters it is equal the maximum value. The number of free adsorption sites calculated for a mass unit of a catalyst is presented in the following sequence: K > Rb > Cs > Na. The calculated, optimal amount of potassium oxide leading to formation of a maximum number of free redox sites is 0.48 wt%.

Owing to the above model, it is possible to explain many properties of iron catalyst. Iron catalysts which contain potassium and no other alkali metals are characterized with the highest catalytic activity. Traditional explanation of how alkaline metals affect the activity of catalysts is based on their influence on electron transport during surface reaction. This approach points out to cesium as the element that best influences an increase of catalytic activity. This point of view is correct for supported catalysts, e.g. ruthenium catalyst for ammonia synthesis [60]. However, in case of iron catalyst, promoting with cesium leads to obtaining a catalyst with worse catalytic properties than that containing potassium. This is due to the fact that although alkali metals form adsorption sites on iron surface, they also influence the size of specific surface area of an already formed catalyst. These two factors overlapping each other affect the final activity of catalyst calculated for mass units. The above model clearly shows that the presence of potassium atoms should lead to formation of an optimal structure of catalyst.

4. APPLICATIONS OF DOUBLE LAYER MODEL

From the double layer model it also follows that any change leading to formation of free surface of iron should be accompanied by covering this new, free surface by an identical layer to that found in other parts of the catalyst. This conclusion was the basis on which an experiment was devised aiming at confirming the state of equilibrium inside iron catalyst. The experiment also made it possible to determine the chemical composition of the surface of iron catalyst by means of electron spectroscopy [61].

It was assumed in the experiment that bringing a real iron catalyst into direct contact with clean iron surface should lead to diffusion of surface constituents and that this area should be covered by a layer identical to that covering catalyst's particles. If free surface of iron introduced into a system were small enough in comparison with the total surface area of catalyst, then a change in composition triggered by its introduction should be negligible. The form of free

surface introduced into a catalytic system should be such, so that it would facilitate investigating the system by means of electron spectroscopy.

To this end a thin iron foil, additionally folded in two, was introduced into a catalytic reactor filled with grains of iron catalyst (Figure 4). Owing to this, only the outer side of the foil came into contact with catalyst's grains and the inner side of the foil could be covered by a layer of promoters only through diffusion of surface constituents. The system was subjected to the influence of nitrogen – hydrogen reaction mixture for 16 hrs, at the temperature of 450°C and under the pressure of 10 MPa. It was supposed to equilibrate compositions of iron foil's surface and the surface of iron catalyst's grains. This process was conducted on several samples of the metal foil and on every occasion foil samples were brought into contact with iron catalyst with a modified content of potassium compounds.

The samples obtained in this way were later transferred to a vacuum chamber of electron spectrometer and both sides of the foil, the one that came into contact with catalyst's grains and the other side that had no contact with them, were investigated by means of AES method.

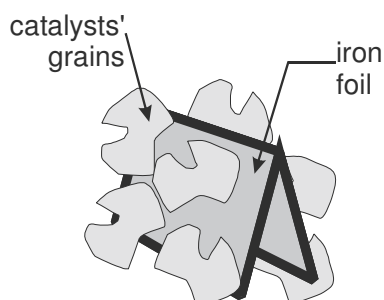


Fig. 4. Iron foil placed among iron catalyst's grains. Its inside part does not touch the catalyst.

It was found that the chemical composition of both sides of the foil is the same and that except iron it also contains a significant amount of oxygen and potassium, which were not to be found on clean iron foils. Small amounts of calcium were also found on the surface of the samples. It was also found that there is a clear correlation between chemical composition of the iron foil investigated by means of electron spectroscopy and the contents of potassium compounds in catalyst determined using chemical analysis methods (Figure 5).

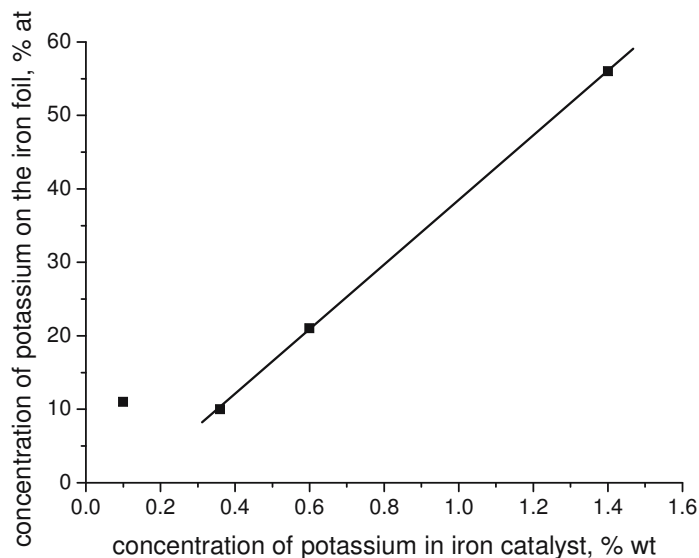


Fig. 5. Potassium concentration on surfaces which did not touch iron catalyst's grains.

The above results seem to suggest that according to the assumptions of the double layer model a diffusion of surface constituents of a catalyst to a new surface of iron does take place. Because AES investigations showed that on the surface of iron foil mostly potassium and oxygen were to be found, it can well be assumed that in a real iron catalyst these two elements constitute the main elements of the surface layer. No traces of aluminum were observed, although it constituted almost 3% of the iron catalyst's mass. Earlier investigations showed that aluminum oxide directly deposited on iron surface spread throughout it freely [62]. The fact that no aluminum was found on the surface of the investigated foil is due to privileged diffusion of potassium ions on iron surface. Aluminum forms its own structures inside catalyst not taking part in forming surface layer, which was suggested in earlier research.

Another experiment was supposed to determine the rate of surface diffusion of potassium from the inside of iron catalyst's grain to the surface of clean iron foil [63, 64]. To this end in the centre of iron foil placed on the sample holder a small grain of iron catalyst was fixed. Next, the system was heated for a dozen or so hours at 400°C in high vacuum conditions. The chemical composition of iron foil's surface along a line passing through catalyst's grain was determined using AES method.

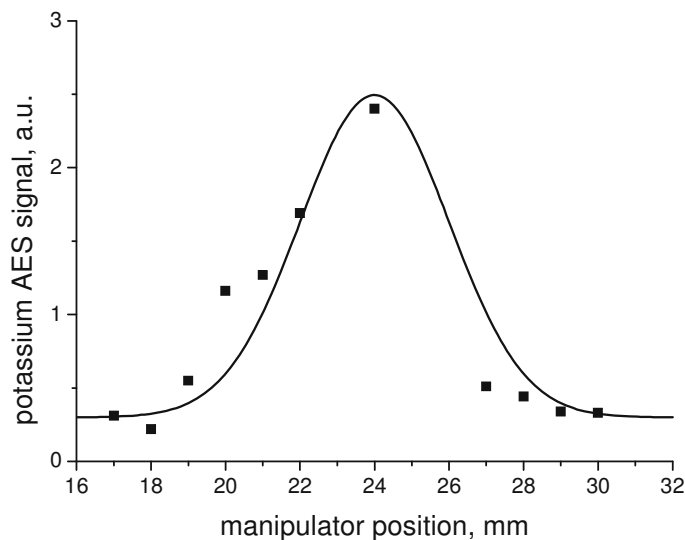


Fig. 6. AES signal of potassium measured on iron foil along a line passing through catalyst's grain. The catalyst's grain is placed in the manipulator's position of 24 mm. The temperature of the heating treatment – 400°C.

Figure 6 presents the intensity of potassium AES signal measured at different places of iron foil after several hours of heating treatment. Before the heating potassium was detected only in catalyst's grain, which was placed in the manipulator's position – 24 mm. After the heating potassium content on iron foil was registered in distances as far as 8 mm from the catalyst's grain. Additionally, potassium AES intensity signal distribution is in accordance with curve characteristic for surface diffusion processes starting from a small point on a surface. It points out to a homogeneous diffusion of potassium atoms in all directions of iron foil's surface. On the basis of a change of potassium AES intensity signal on time a coefficient of potassium diffusion on the surface of iron foil was calculated.

On the basis of the double layer model of iron catalyst it can also be pointed out that substituting oxygen atoms stabilizing potassium atoms present on iron surface by atoms stronger binding with iron should lead to a decrease of potassium's thermal stability. Investigations on iron surface covered by a layer containing potassium and oxygen and then subjected to hydrogen sulfide exposure point out to a significant decrease of potassium content in the surface covered by sulphur.

Figure 7 presents AES spectra of iron foil heated at 400°C. The spectrum marked as B corresponds to a surface covered by a layer containing oxygen and

potassium atoms. After several hours of heating it at 400°C no significant changes of surface composition of this sample were recorded. Later on the sample was subjected to hydrogen sulfide and it was next heated at 400°C. An approximately three-fold decrease of potassium AES intensity signal was observed. Additionally, an almost complete lack of AES signal from oxygen was observed. This points out to a process of removing oxygen atoms from iron surface. A lack of stabilizing force of oxygen atoms lead, as a result, to potassium desorption from iron surface.

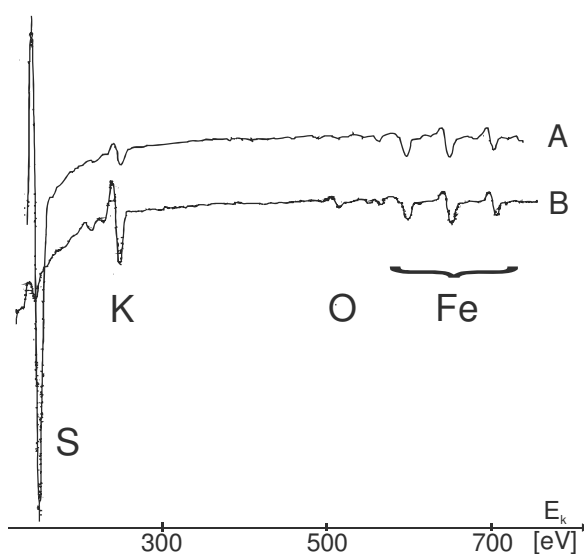


Fig. 7. AES spectra of iron foil covered by potassium and oxygen. Spectrum A – heating at 400°C after hydrogen sulfide's exposure, spectrum B – heating at 400°C.

5. CONCLUSIONS

The above presented short outline of investigations of iron catalyst by means of electron spectroscopy methods shows that these methods have a significant advantage in developing models of this catalyst's structure and in explaining mechanisms of reactions occurring on its surface. The presented model of the catalyst's surface, the so-called double layer model, makes it possible to explain a number of various properties of the catalyst. Its development and experimental validation of the catalyst's operation would not be possible without techniques of investigating surface of solids, and particularly without techniques of electron spectroscopy.

6. REFERENCES

- [1] A. Nielsen, *An Investigation on Promoted Iron Catalysts for Synthesis of Ammonia*, Jul. Gjellerups Forlag, Copenhagen, 1968.
- [2] J.R. Jennings, Plenum Press, New York, 1991.
- [3] K. Altenburg, et al., *J. Catal.*, 66 326 (1980).
- [4] W. Arabczyk, *Polish J. Chem.*, 7 8 (2005).
- [5] S.R. Bare, D.R. Strongin, and G.A. Somorjai, *J. Phys. Chem.*, 90 4726 (1986).
- [6] H. Bosch, J.G.v. Ommen, and P.J. Gellings, *Appl. Catal.*, 18 405 (1985).
- [7] M.E. Dry, J.A.K.d. Plessis, and G.M. Leuteritz, *J. Catal.*, 6 194 (1966).
- [8] K. Engvall, et al., *Appl. Catal. A: General*, 134 239 (1996).
- [9] G. Ertl, M. Weiss, and S.B. Lee, *Chem. Phys. Lett.*, 60 391 (1979).
- [10] Z. Kowalczyk, et al., *Appl. Catal. A: General*, 87 1 (1992).
- [11] K.C. Waugh, D.A. Butler, and B.E. Hayden, *Top. Catal.*, 1 43 (1994).
- [12] H.-C. Chen and R.B. Anderson, *J. Coll. Interf. Sci.*, 38 535 (1972).
- [13] P.B. Sewell, D.F. Mitchell, and M. Cohen, *Surf. Sci.*, 33 535 (1972).
- [14] C. Leygraf and S. Ekelund, *Surf. Sci.*, 40 609 (1973).
- [15] A.J. Melmed and J.J. Carroll, *J. Vac. Sci. Technol.*, 10 164 (1973).
- [16] T. Horiguchi and S. Nakanishi, *Japan. J. Appl. Phys. Suppl.*, 2 89 (1974).
- [17] M. Watanabe, et al., *Japan. J. Appl. Phys. Suppl.*, 2 501 (1974).
- [18] G. Ertl and K. Wandelt, *Surf. Sci.*, 50 479 (1975).
- [19] K. Kunimori, et al., *Surf.Sci.*, 59 302 (1976).
- [20] K.Y. Yu, et al., *Surf. Sci.*, 57 157 (1976).
- [21] F. Bozso, et al., *J. Catal.*, 49 18 (1977).
- [22] F. Bozso, et al., *Appl. Surf. Sci.*, 1 103 (1977).
- [23] F. Bozso, G. Ertl, and M. Weiss, *J. Catal.*, 50 519 (1977).
- [24] G. Broden, G. Gafner, and H.P. Bonzel, *Appl. Phys.*, 13 333 (1977).
- [25] G. Ertl, et al., *Chem. Phys. Lett.*, 52 309 (1977).
- [26] H.J. Grabke, et al., *Surf.Sci.*, 63 377 (1977).
- [27] K. Kishi and M.W. Roberts, *Surf. Sci.*, 62 252 (1977).
- [28] M. Grunze, et al., *Appl. Surf. Sci.*, 1 241 (1978).
- [29] K. Yoshida and G.A. Somorjai, *Surf.Sci.*, 75 46 (1978).
- [30] W. Arabczyk, H.J. Muessig, and F. Storbeck, *Phys. Stat. Solid. A*, 55 437 (1979).
- [31] W. Arabczyk and H.J. Muessig, *Vacuum*, 37 137 (1985).
- [32] D.W. Johnson and M.W. Roberts, *Surf. Sci.*, 87 L255 (1979).
- [33] G. Ertl, et al., *Appl. Surf. Sci.*, 8 373 (1981).
- [34] G. Ertl, S.B. Lee, and M. Weiss, *Surf. Sci.*, 114 527 (1982).
- [35] W. Arabczyk, E. Rausche, and F. Storbeck, *J. Elec. Spectr. Rel. Phenomen.*, 53 107 (1990).
- [36] W. Arabczyk, E. Rausche, and F. Storbeck, *Surf. Sci.*, 247 264 (1991).
- [37] W. Arabczyk, E. Rausche, and F. Storbeck, *Acta.Phys. Pol.A*, 81 109 (1992).
- [38] P.E.H. Nielsen, in *Catalytic Ammonia Synthesis, Fundamentals and Practice*, J.R. Jennings, ed., Plenum Press, New York, 1991, p 285.
- [39] G. Broden and H.P. Bonzel, *Surf. Sci.*, 84 106 (1979).
- [40] G. Pirug, G. Broden, and H.P. Bonzel, *Surf. Sci.*, 94 323 (1980).
- [41] S.B. Lee, M. Weiss, and G. Ertl, *Surf. Sci.*, 108 357 (1981).
- [42] Z. Paal, G. Ertl, and S.B. Lee, *Appl. Surf. Sci.*, 8 231 (1981).
- [43] H.P. Bonzel, G. Broden, and H.J. Krebs, *Appl. Surf. Sci.*, 16 373 (1983).
- [44] W. Arabczyk, et al., in *Symposium on Surface Science*, Centre National de la Recherche Scientifique, La Plagne, France, 1992, pp 260.
- [45] W. Arabczyk, et al., *Appl. Surf. Sci.*, 72 45 (1993).

- [46] W. Arabczyk and U. Narkiewicz, *Polish J. Chem.*, 69 1054 (1995).
- [47] W. Arabczyk and U. Narkiewicz, *Surf. Sci.*, 377-379 578 (1997).
- [48] W. Arabczyk, U. Narkiewicz, and D. Moszyński, *Appl. Catal. A: General*, 182 379 (1999).
- [49] G. Ertl and N. Thiele, *Appl. Surf. Sci.*, 3 99 (1979).
- [50] G. Ertl, S.B. Lee, and M. Weiss, *Surf. Sci.*, 111 L711 (1981).
- [51] G. Ertl, S.B. Lee, and M. Weiss, *Surf. Sci.*, 114 515 (1982).
- [52] G. Ertl, *J. Vac. Sci. Technol. A*, 1 1247 (1983).
- [53] G. Ertl, et al., *J. Catal.*, 79 359 (1983).
- [54] N.D. Spencer, R.C. Schoonmaker, and G.A. Somorjai, *J. Catal.*, 74 129 (1982).
- [55] D.R. Strongin, et al., *J. Catal.*, 103 213 (1987).
- [56] D.R. Strongin, S.R. Bare, and G.A. Somorjai, *J. Catal.*, 103 289 (1987).
- [57] G. Ertl, *Catal. Rev. Sci. Eng.*, 21 201 (1980).
- [58] M. Boudart, *Catal. Rev. Sci. Eng.*, 23 1 (1981).
- [59] W. Arabczyk, U. Narkiewicz, and D. Moszyński, *Langmuir*, 15 5785 (1999).
- [60] K. Urabe, K. Shiratori, and A. Ozaki, *J. Catal.*, 55 71 (1978).
- [61] W. Arabczyk, et al., *Stud. Surf. Sci. Catal.*, 130 3113 (2000).
- [62] G. Connell and J.A. Dumesic, *J. Catal.*, 92 17 (1985).
- [63] U. Narkiewicz, D. Moszyński, and M. Broślawski, *Rev. Adv. Mater. Sci.*, 8 37 (2004).
- [64] U. Narkiewicz, D. Moszyński, and M. Broślawski, *Appl. Surf. Sci.*, 252 833 (2005).

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