Catalysis Today 169 (2011) 97–101

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Measurements of the relative number of active sites on iron catalyst for ammonia synthesis by hydrogen desorption

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ARTICLE INFO

Article history:
Available online 5 October 2010

Keywords:
Active surface area
Ammonia synthesis iron catalyst
Nanocrystalline iron
H_2-TPD

ABSTRACT

Analysis of relative number of active sites of ammonia synthesis iron catalysts was performed by TPD-H_2 method. Samples of the industrial pre-reduced catalyst, which were reduced and heated at different temperatures from the range 500 °C to 780 °C in order to modify their specific surface area, were used. Chemical composition of samples to be tested was modified as well by adding sulfur compound or reducing the amount of potassium oxide. The process of hydrogen adsorption was conducted at 25 °C. Then hydrogen adsorption occurs on the surface together with absorption in the volume of iron. On the spectrum of H_2-TPD the presence of peaks α_1, α_2 and α_3 was observed at temperatures 130 °C, 300 °C and 450 °C, respectively. Peak α_1, associated with adsorption on the surface, is proportional to the total amount of absorbed as well as adsorbed hydrogen. Height of α_1 peak varies with the shift of catalysts' activity. This peak gives the information about the number of active sites on the catalyst's surface. Heights of peaks α_2 and α_3 depend mainly on the size of sorption of hydrogen in the volume of iron. Changes in activity of the samples did not significantly affect the heights of peaks α_2 and α_3.

1. Introduction

Active and specific surface area of catalyst are important parameters which characterize its functioning. Knowledge about the structure of the catalyst present under the process conditions (composition of the gas phase, high temperature and pressure) is not fully understood. Specific surface area is determined mostly by the BET method based on low-temperature adsorption of nitrogen [1,2]. In the case of supported catalysts a standard procedure is to determine the number of active sites on the catalyst surface and the average crystallite size on the basis of measurements of hydrogen chemisorption [3,4]. On the metallic phase, hydrogen can adsorb both reversibly and irreversibly, however, it is excluded that it is possible to adsorb hydrogen by any type of adsorption on catalyst's support [5]. Hydrogen on metals is adsorbed by means of dissociative adsorption, and each of the dissociated hydrogen atoms is adsorbed on one surface metal atom [3,4]. Application of chemisorptive procedure using hydrogen for the tests of Pt, Pd, Rh, Ru, Ir, Fe, Ni and Co deposited on the support phase has been fully described in the literature [3,4,6,7]. Determination of active surface area of fused iron catalysts by means of thermo-programmed desorption of hydrogen has been described [8,9].

For the determination of active surface area of metals the process of adsorption of oxygen or carbon monoxide can be also applied. In the case of oxygen adsorption on metals a high probability of formation of multiple layers of metal oxide should be considered [5]. From the description of oxygen interactions with the surface of iron catalyst at a temperature of −183 °C [1] it can be concluded that even in such a low temperature apart from oxygen chemisorption also oxidation of a few layers of iron atoms takes place. To reduce these effects only to chemisorption, small partial pressures of oxygen are applied [10–12]. In turn, the adsorption stoichiometry of carbon monoxide on metal catalysts is characterized by high variety. On the one hand, there is a possibility that a CO molecule bounds to 2–4 metal atoms, on the other hand it is possible that the 2–3 CO molecules adsorb on a single metal atom [5]. The adsorptive structure of CO-metal depends on the type of metal and its surface structure, the increase in metal dispersion on a support makes a clear increase in the number of CO molecules adsorbed on one metal atom. Due to these facts, the usefulness of the CO chemisorption for measurement of the active surface are of catalysts is limited. Measurements by these described methods are carried out at atmospheric pressure following the stop or freeze the reduction process, which means that the actual form of the catalyst under (real) reaction conditions is different from that which can be analyzed by classical methods.

The method for determining the active surface area of the iron catalyst by dosing of small quantities of oxygen or carbon monoxide to a mixture of hydrogen and nitrogen in ammonia synthesis

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doi:10.1016/j.cattod.2010.09.003

conditions was presented [13]. The use of a reversible poison, however, means that it is not possible to determine the exact amount of the poison on the catalyst's surface.

Sulfur is a durable poison of iron catalyst [14] and at low concentrations of sulfur it chemisorbs only on the active sites [15]. On the basis of this phenomenon a method was proposed [16] for determining the active surface area of iron catalyst during the ammonia synthesis, catalytic decomposition of ammonia and catalytic decomposition of methane. It was assumed that a sulfur atom chemisorbs on one active site, therefore, the number of sulfur atoms on the catalyst's surface is equal to the number of poisoned active sites. It has been shown that the relative number of active sites in the synthesis and the decomposition of ammonia and the reaction of carburization increased with increasing temperature [16].

Based on previous studies it was found that the activity of the catalyst in the synthesis of ammonia depends on the active surface area, rather than on the specific surface area. Comparing the temperature dependence of the specific surface area with ability of the catalyst to chemisorption of oxygen it can be concluded that on the catalyst with the largest specific surface area the smallest amount of oxygen could be adsorbed [17].

Pre-reduced iron catalyst for ammonia synthesis has a nanocrystalline structure. Iron crystallites being an active element in the catalyst are of the size of tens of nanometers [18]. The structure of the catalyst has been the subject of many studies and is described in the monographs [18–21]. It was found that it is stable at high temperatures due to the presence of structure-promoters [22–28], which form bridges between iron nanocrystallites. It was also found that the spatial structure of the catalyst depends on the temperature. Stable structure at a given temperature does not change at temperatures lower than the temperature of stabilization [29]. Potassium oxide is a promoter, which increases the activity of the catalyst in the synthesis of ammonia. According to the model of the active surface of iron ammonia synthesis catalyst [30,31] the presence of the alkali metal oxides (mainly potassium oxide) contributes to the increase of the number of active sites. This promoter does not create a solid solution in the iron, but is located in the spaces between the iron crystallites and wets the surface of crystallites. Potassium oxide from the geometrical reasons causes the increase of the number of active sites. The active surface area is approximately 50% of the specific surface area of the catalyst [31].

The purpose of this study is to search for correlation between results obtained by the thermo-programmed desorption of hydrogen method and the information on activity of the catalyst in the ammonia synthesis conditions, known from the literature.

2. Experimental

The studies were conducted on a pre-reduced industrial iron catalyst. The chemical composition of the catalyst was determined by atomic emission spectrometry with inductively coupled plasma (ICP-AES) using Optima 5300DV apparatus (Perkin Elmer). In addition to a metallic iron the catalyst contained 3.3 wt% Al_2O_3, 2.8 wt.% CaO and 0.65 wt.% K_2O. By rinsing the catalyst with water, the concentration of potassium oxide was reduced to 0.1 wt.%, calcium oxide to 2.66 wt.%, while the aluminum oxide content did not change. To the portion of the industrial iron catalyst the sulfur compound was introduced from the liquid phase and samples containing 350 ppm *S* and 3500 ppm *S* were obtained.

Temperature-programmed desorption processes of hydrogen (H_2-TPD) were carried out in a system with differential reactor and TCD detector [32]. Gases of high purity (99.999%) flowed through the reactor. The gases were additionally purified using columns filled with palladium–copper catalyst, manganese catalyst and molecular sieves, respectively.

As a result of previous studies [32] concerning the effect of annealing temperature on the structure of the catalyst, the fixed dependence of the specific surface area on temperature of annealing of the catalyst was presented. Taking into account that information, the specific surface areas of all tested samples of the industrial iron catalyst, depending on the annealing temperature, were determined. Catalysts were reduced with the mixture of 10% H_2/Ar, flowing at a rate of 40 ml/min, with temperature gradient 5 °C/min. Samples of the catalysts of the stable specific surface areas (which were not changed by temperature-programmed desorption of hydrogen) were obtained, after determining the maximum temperature of the reduction process, T_{max}, with specified chemical compositions of samples. In parentheses is the temperature, T_h, and time, *t*, of the isothermal heating process of samples – followed by measurement by the temperature-programmed desorption of hydrogen:

- $S = 4\ m^2\ g^{-1}$ ($T_{max} = 700\ °C$) for industrial catalyst and for industrial catalyst poisoned with sulfur ($T_h = 525\ °C$, $t = 12\ h$);
- $S = 10\ m^2\ g^{-1}$ ($T_{max} = 700\ °C$) for catalyst containing 0.1 wt.% K_2O ($T_h = 525\ °C$, $t = 12\ h$).

TPD-H_2 measurements were also performed changing the specific surface area of samples (*S* from $12.5\ m^2\ g^{-1}$ to $4\ m^2\ g^{-1}$) by establishing a maximum reduction temperature (T_h in the range from 500 °C to 780 °C) the same as for the hydrogen thermodesorption process.

Reduced catalysts were heated in argon atmosphere and at temperature of reduction in order to remove hydrogen from the catalyst surface, and then quickly cooled down to room temperature. Sorption of hydrogen was carried out at 25 °C for 0.5 h. After the sorption process the sample of catalyst was rinsed with argon to remove weakly bounded hydrogen from the catalyst surface. An exception to this practice was to examine the industry catalyst by H_2-TPD performed without the high temperature annealing in argon stage before the adsorption of hydrogen. Desorption of hydrogen was performed in the flow of 40 ml/min of argon with linear gradient of temperature (20 °C/min) to such a temperature as the maximum reduction temperature of catalysts was.

3. Results and discussion

Fig. 1 shows the course of temperature-programmed desorption of hydrogen for the reduced industrial iron catalyst. The first H_2-TPD measurement was performed immediately after reduction, so the sample was saturated with hydrogen, while the second measurement was performed on the catalyst after the heating of the sample in an atmosphere of argon and subsequent hydrogen adsorption at 25 °C (adsorption of hydrogen on the catalyst's surface).

H_2-TPD spectrum of hydrogen adsorbed on the catalyst surface is composed of three peaks at temperatures 130 °C, 300 °C and 450 °C, whose presence indicates the existence of three adsorption states on the catalyst surface. Similar spectra is presented in [9], and are marked with the symbols α_1, α_2 and α_3 (in the present study the same symbols are used).

The desorption profile obtained for the hydrogen desorption from the catalyst surface together with hydrogen absorbed (spectrum B) contains also characteristic peaks α_1 and α_2, whose position is similar, and the difference is the amount of hydrogen desorbed as compared to spectrum A.

In the figure above the difference between the hydrogen desorption spectra, obtained for sample saturated with hydrogen, and sample where hydrogen was adsorbed only on the surface, is presented (dashed line). The area under this curve approximately

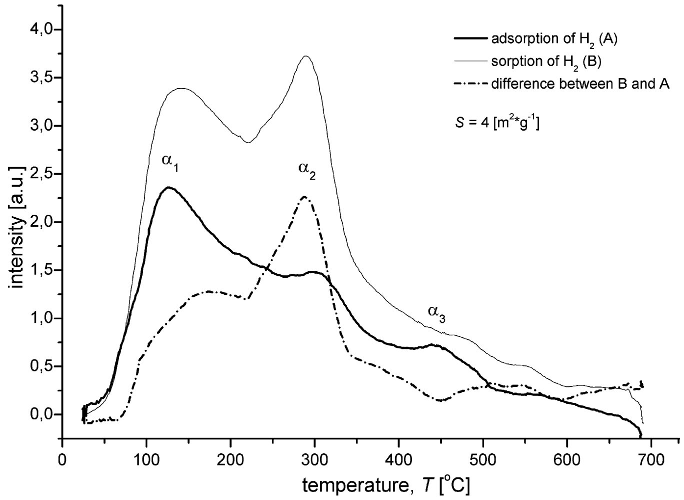

Fig. 1. H_2-TPD spectra for the reduced industrial iron catalyst: sample with H_2 adsorbed on the surface (A), sample saturated with H_2 (B), difference between B and A (T_{max} = 700 °C, T_h = 525 °C, t = 12 h).

corresponds to the amount of hydrogen dissolved in a volume of catalyst. Hydrogen dissolved in the sample volume is desorbed in the whole temperature range of TPD spectrum, but this part of hydrogen has a much greater influence on the height of the peak α_2 in comparison to the peak α_1. On this basis, peak α_1 can be attributed to desorption of hydrogen adsorbed mainly on the surface iron atoms, while the intensity of the α_2 and α_3 is the sum of hydrogen adsorbed on the surface and absorbed in the iron volume due to the increase in temperature.

Properly long annealing of the reduced iron catalyst in a hydrogen atmosphere at a given temperature causes the formation of a stable structure of the catalyst of certain size of the specific surface area. Specific surface area of the iron catalyst reduced at temperature 500 °C is 12 $m^2 g^{-1}$. The increase in temperature of the reductive annealing to 720 °C causes that the specific surface area is reduced to 4 $m^2 g^{-1}$ [32].

In order to measure the total amount of hydrogen absorbed and adsorbed, in the initial stage the thermo-programmed desorption was conducted polythermally, and then the rest of hydrogen was desorbed isothermally (Fig. 2). The area under the desorption curve is the measure of the amount of hydrogen absorbed and adsorbed.

H_2-TPD spectra recorded during the study of the influence of temperature on adsorption of hydrogen on the surface of iron catalyst is shown in Fig. 3. Intensities of the peaks α_1 and α_2 decrease with the decrease of the surface area, and their ratio increases. In the H_2-TPD spectra for catalysts with surface areas less than 4 $m^2 g^{-1}$ the peak α_2 disappears while the peak α_3 becomes more distinct.

The dependence of the peak α_1 intensity on the total volume of adsorbed hydrogen referred to 1 g of catalyst can be described by a linear function (Fig. 4).

Chemical composition of samples is stable by 700 °C. Therefore for further analysis the data obtained at temperatures less than 700 °C were selected. In Fig. 5 the intensity of peak α_1, which is supposed to be a measure of catalyst's activity, was plotted as a function of surface area achieved at different temperatures. The data presented in the plot above show that the desorption of hydrogen at 130 °C decreases with decrease of catalyst surface area.

Changes in the total volume of adsorbed hydrogen, converted per unit of area of the catalyst surface, depending on the specific surface area achieved in each of the temperatures are shown in Fig. 6. Adsorption of H_2 per unit of catalyst surface increases with the decrease in specific surface area. Concentration of free adsorption sites, C_a, is determined by means of ratio of the number of adsorption sites occupied by hydrogen atoms to total number of surface iron atoms. The concentration of free adsorption sites tends to decrease with increasing specific surface area in the range of C_a = 0.60 (specific surface area 4.3 m^2/g) to C_a = 0.42 (specific surface area 12 m^2/g).

The introduction of sulfur compounds to the iron catalyst causes permanent deactivation of the catalyst. Research on the influence of sulfur concentration on the activity of iron catalysts are presented in [16]. Reduction in catalytic activity in ammonia synthesis reaction depends on the concentration of poison and on the temperature of the process.

H_2-TPD curves obtained for two samples of iron catalyst poisoned with different amounts of sulfur are presented in Fig. 7. For reference purposes the figure shows the profile of H_2-TPD for iron catalyst without poison. Peak α_1 for the sample with 350 ppm sulfur is broad and far lower in comparison to the clearly outlined peak α_2. Almost complete poisoning of the catalyst (3500 ppm S) causes that the intensity of peak α_1 becomes vanishingly small, while the height of the peak α_2 in a relatively small degree differs

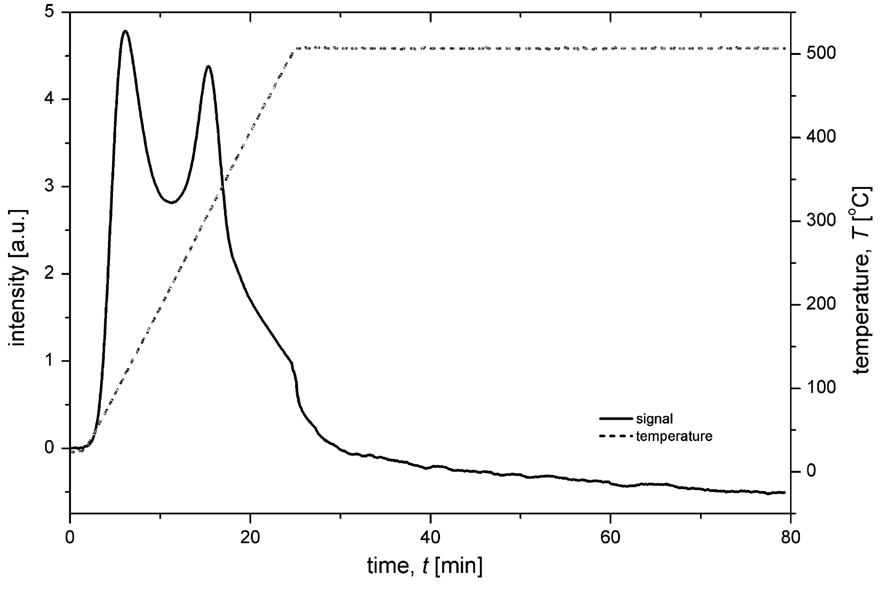

Fig. 2. H_2-TPD spectrum for the reduced industrial iron catalyst and temperature as functions of time.

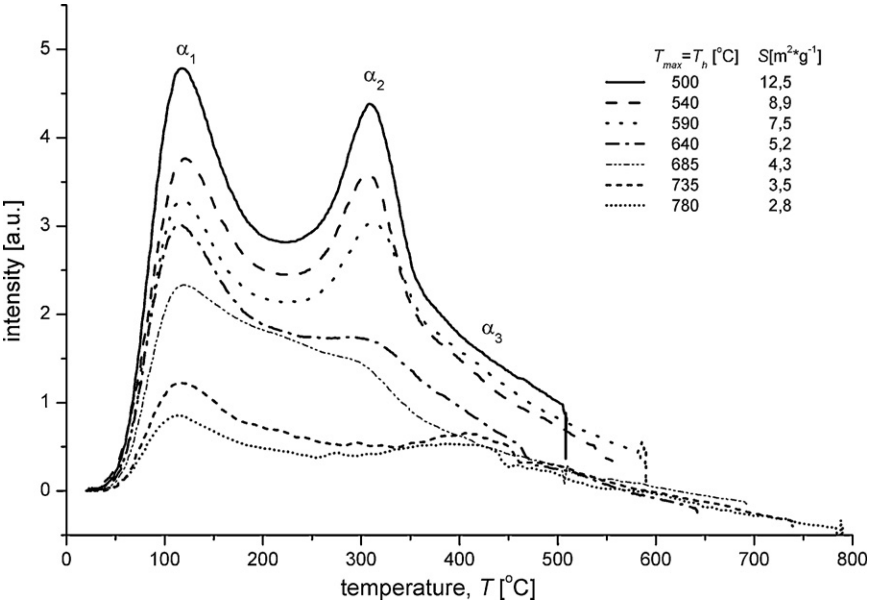

Fig. 3. H_2-TPD spectra for the reduced industrial iron catalyst as functions of temperature.

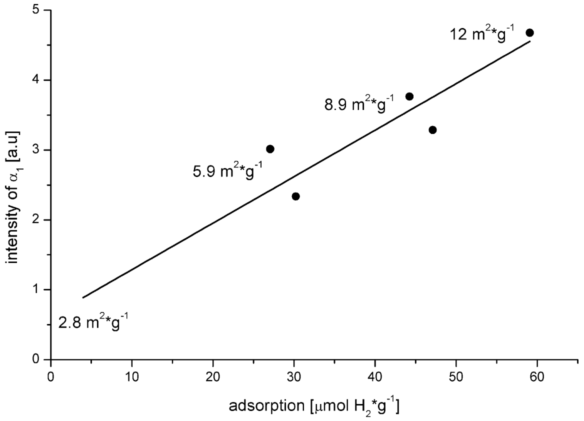

Fig. 4. Intensity of peak α_1 as a function of the total volume of adsorbed hydrogen (referred to the 1 g of catalyst).

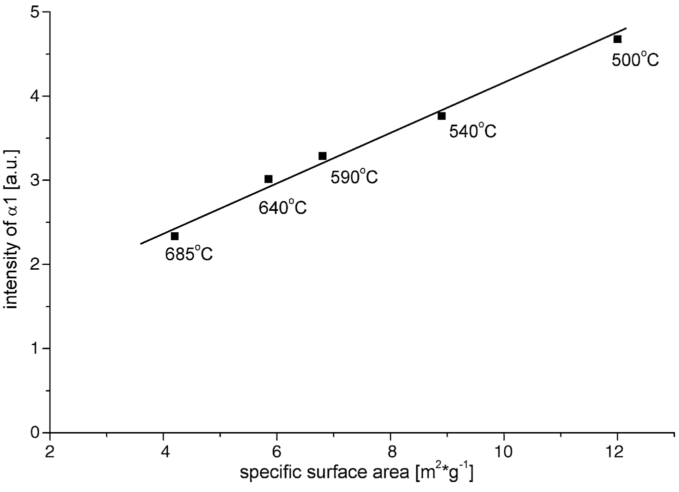

Fig. 5. Intensity of peak α_1 as a function of the specific surface area of iron catalyst.

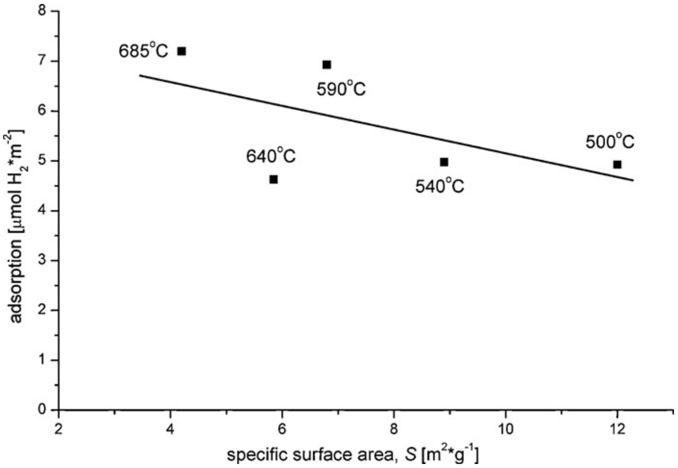

Fig. 6. Total volume of adsorbed hydrogen as a function of the specific surface area of iron catalyst.

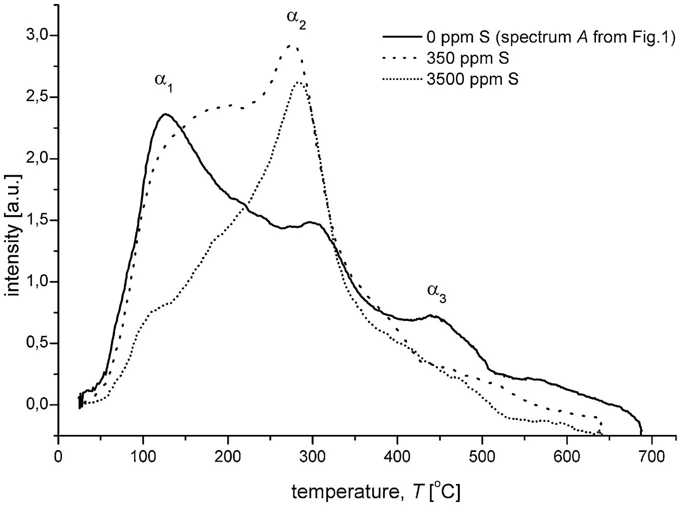

Fig. 7. H_2-TPD spectra for the reduced industrial iron catalyst: samples poisoned with sulfur and spectrum A from Fig. 1 as a reference sample ($T_{\mathrm{max}} = 700\,^\circ\mathrm{C}$, $T_{\mathrm{h}} = 525\,^\circ\mathrm{C}$, $t = 12$ h).

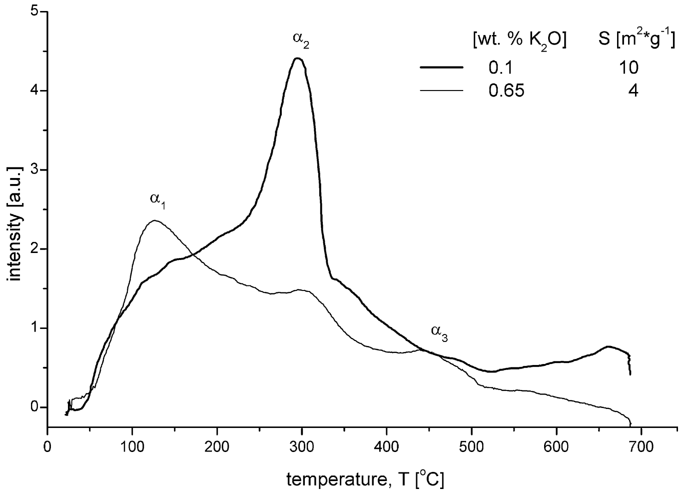

Fig. 8. H_2-TPD spectra for the reduced industrial iron catalyst: sample with 0.1 wt.% K_2O and spectrum A from Fig. 1 as a reference sample (0.65 wt.% K_2O) (T_{max} = 700 °C, T_h = 525 °C, t = 12 h).

from the intensity of that peak for the catalyst with 10-fold lower sulfur content.

Catalytic activity of iron in the synthesis of ammonia is significantly determined by the concentration of potassium oxide. The effect of alkali promoter on the rate of the reaction is similar regardless of whether potassium is introduced before the fusing of the charge of catalyst's precursor [33], or is embed directly on the surface of the pre-reduced catalyst by impregnation method [34,35]. With the growing amount of potassium oxide to about 0.65 wt.% the increase in catalytic activity was observed. When the concentration of 0.8 wt.% K_2O is exceeded, the catalytic activity decreases. With increasing potassium content the specific surface area of catalyst decreases from 10 $m^2\,g^{-1}$ for 0.1 wt.% K_2O to 4 $m^2\,g^{-1}$ for 0.65 wt.% K_2O.

H_2-TPD spectrum of a catalyst with the reduced amount of potassium oxide is shown in Fig. 8. Compared to the industrial catalyst heated in 700 °C the catalyst with the reduced amount of potassium oxide is of approximately 2-fold greater specific surface area. With the increase of the specific surface area, increases the total amount of adsorbed hydrogen. Reducing the concentration of K_2O from 0.65 to 0.1 wt.% leads to a significant reduction of the α_1 peak intensity with respect to the α_2 peak intensity. The obtained spectrum has a shape comparable to the H_2-TPD spectra obtained for the catalysts, which are deactivated by poisoning.

4. Conclusions

The H_2-TPD profile consists of peaks originating from hydrogen adsorbed on the surface of iron and hydrogen, which has been dissolved in the mass of catalyst.

H_2-TPD spectra of catalysts with low catalytic activity (low potassium content, or poisoned with sulfur) are characterized by a decrease in α_1 to α_2 peak height ratio. The height of peak α_1 is less affected by part of hydrogen absorbed in the sample volume. As a result of segregation of hydrogen on the surface of the sample, it also creates a state of adsorption corresponding to peak α_2 in the H_2-TPD spectrum. These statements allow the conclusion that the intensity of peak α_1 which comes mainly from hydrogen adsorbed on the surface of iron is a measure of the relative number of free adsorption sites, i.e. of the active surface of catalyst.

Reducing of the specific surface area of the catalyst is accompanied by an increase of concentration of active sites on the catalyst surface.

References

[1] S. Brunauer, P.H. Emmett, J. Am. Chem. Soc. 59 (1937) 1553.
[2] S. Brunauer, P.H. Emmett, J. Am. Chem. Soc. 62 (1940) 1732.
[3] C.H. Bartholomew, Catal. Lett. 7 (1990) 27.
[4] C.H. Bartholomew, in: J. Spivey (Ed.), Catalysis, Royal Society of Chemistry, Cambridge, 1994.
[5] R.J. Farrauto, C.H. Bartholomew, Fundamentals of Industrial Catalytic Processes, Blackie Academic& Professional, 1997.
[6] R.J. Farrauto, AIChE Symp. Ser. 70 (143) (1974) 9.
[7] J.L. Lemaitre, P.G. Menon, F. Delannay, in: F. Delannay (Ed.), Charakterization of Heterogeneous Catalysts, Marcel Dekker, New York, 1984.
[8] J. Zieliński, L. Znak, Z. Kowalczyk, Pol. J. Chem. 75 (2001) 1927.
[9] L. Huazhang, L. Caibo, L. Xiaonian, C. Yaqing, Ind. Eng. Chem. Res. 42 (2003) 1347.
[10] M. Arbab, J.B. Hudson, Surf. Sci. 206 (1988) 317.
[11] A. Hodgson, A. Wight, G. Worthy, Surf. Sci. 319 (1994) 119.
[12] V.S. Smentkowski, Y.T. Yates, Surf. Sci. 232 (1990) 113.
[13] K.C. Waugh, D.A. Butler, B.E. Hayden, Catal. Lett. 24 (1994) 197.
[14] J. Benard, J. Oudar, N. Barbouth, E. Margot, Y. Berthier, Surf. Sci. 88 (1979) L35.
[15] C.H. Bartholomew, P.K. Agrawal, J.R. Katzer, Adv. Catal. 31 (1982) 136.
[16] W. Arabczyk, D. Moszyński, U. Narkiewicz, R. Pelka, M. Podsiadły, Catal. Today 124 (2007) 43.
[17] I. Jasińska, K. Lubkowski, W. Arabczyk, Przem. Chem. 82/3 (2003) 230.
[18] J.R. Jennings (Ed.), Catalytic Ammonia Synthesis Fundamentals and Practice, Plenum Press, New York, 1991.
[19] W.G. Frankenburg, in: P.H. Emmet (Ed.), Catalysis, vol. 3, Reinhold, New York, 1955.
[20] A. Nielsen, An Investigation on Promoted Iron, Jul. Gjellerups Forlag, 1968.
[21] A. Nielsen (Ed.), Ammonia, Catalyst and Manufacture, Springer-Verlag, Berlin, 1995.
[22] G. Ertl, in: J.R. Jennings (Ed.), Catalytic Ammonia Synthesis Fundamentals and Practice, Plenum Press, New York, 1991.
[23] G. Ertl, in: T. Inui (Ed.), Successful Design of Catalysts, Elsevier, Amsterdam, 1998.
[24] G. Ertl, S.B. Lee, M. Weiss, Surf. Sci. 114 (1982) 527.
[25] M. Figurski, W. Arabczyk, Z. Lendzion-Bieluń, R.J. Kaleńczuk, S. Lenart, Appl. Catal. A: Gen. 247 (2003) 9.
[26] M. Figurski, W. Arabczyk, Z. Lendzion-Bieluń, S. Lenart, Appl. Catal. A: Gen. 266 (2004) 11.
[27] Z. Lendzion-Bieluń, W. Arabczyk, Appl. Catal. A: Gen. 207 (2001) 37.
[28] Z. Lendzion-Bieluń, W. Arabczyk, M. Figurski, Appl. Catal. A: Gen. 227 (2002) 255.
[29] W. Arabczyk, I. Jasińska, Przem. Chem. 85/2 (2006) 130.
[30] W. Arabczyk, U. Narkiewicz, K. Kałucki, Vacuum 45 (1994) 267.
[31] W. Arabczyk, U. Narkiewicz, D. Moszyński, Langmuir 15/18 (1999) 5785.
[32] I. Jasińska, W. Arabczyk, Chem. Pap. 59 (6b) (2005) 496.
[33] L.M. Dmitrienko, Proc. 4th Int. Congr. Catalysis, Moscow, Nauka, 1, 1970, p. 328.
[34] Z. Kowalczyk, S. Jodzis, Przem. Chem. 66 (1987) 279.
[35] J. Jasińska, Z. Lendzion-Bieluń, W. Arabczyk, Przem. Chem. 89 (2010) 406.