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CHARACTERIZATION OF FeCo BASED CATALYST FOR AMMONIA DECOMPOSITION. THE EFFECT OF POTASSIUM OXIDE

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Abstract

FeCo fused catalyst was obtained by fusing iron and cobalt oxides with an addition of calcium, aluminium, and potassium oxides (CaO, Al_2O_3, K_2O). An additional amount of potassium oxide was inserted by wet impregnation. Chemical composition of the prepared catalysts were determined with an aid of XRF method. On the basis of XRD analysis it was found that cobalt was built into the structure of magnetite and solid solution of $CoFe_2O_4$ was formed. An increase in potassium content develops surface area of the reduced form of the catalyst, number of adsorption sites for hydrogen, and the ammonia decomposition rate. The nitriding process slows down the ammonia decomposition.

Introduction

Intensive investigations over hydrogen usage as a source for energy production are being conducted currently. Hydrogen application encompasses energy production in fuel cells, in stationary as well as portable. The fuel cells applications in transport means seem to be especially promising [1]. Hydrogen production in the ammonia decomposition reaction in comparison with conventional methods as steam reforming, coal gasification, and biomass catalytic gasification has some advantages. The first of all hydrogen from the ammonia decomposition contains no CO_x, which have poisoning impact on catalysts for fuel cells [2]. Liquid ammonia may be easier stored, in comparison with hydrogen [1]. Infrastructure for ammonia production is developed very well and technology of ammonia is well known.

1. Schlapbach, L.; Züttel, A.; Hydrogen-storage materials for mobile applications. *Nature*, **2001**, *414*, 353-358.
2. Chellappa, A.S.; Fischer, C.M.; Thomson, W.J.; Ammonia decomposition kinetics over Ni-Pt/Al$_2$O$_3$ for PEM fuel cell applications. *Appl. Catal.* A, **2002**, *227*, 231-240.

Experimental

❖ Fe-Co fused catalyst was obtained by fusing magnetite with an addition of calcium, aluminium, and potassium oxides (CaO, Al_2O_3, K_2O). During the melting process cobalt(II, III) oxide was added

❖ In order to increase a content of potassium in the catalyst, catalyst was impregnated with water solution of KOH.

❖ Before the ammonia decomposition and the nitriding tests, catalyst was reduced with pure hydrogen at 600^oC.

❖ A series of kinetic measurements of the nitriding process was made for 100% ammonia at a reactor inlet and next nitrides reduction with pure hydrogen at 400^oC.

❖ Activity tests of the catalyst in the ammonia decomposition reaction were carried out in a differential reactor connected with thermogravimeter.

Experimental

❖ Measurements of catalysts activity were performed in the temperature range from 400 to 600°C under ambient pressure.

❖ The ammonia decomposition reaction was tested in the range of ammonia concentration at the reactor inlet from 0 to 100%. Total gas flow was constant – 200 sccm.

❖ Changes of the gas phase, ratio NH_3/H_2, at the reactor inlet were made after reaching a stationary state and when all tests at these conditions were made.

❖ The concentration of hydrogen at the outlet of the reactor was measured on the basis of the thermal conductivity of gas and the concentration of hydrogen assuming stoichiometric decomposition of ammonia at the stationary state [6].

6. Lendzion-Bielun, Z.; Pelka, R.; Arabczyk, W. Study of the Kinetics of Ammonia Synthesis and Decomposition on Iron and Cobalt Catalysts. *Catal. Lett.* **2009**, *129*, 119–121.

Experimental

Conversion degree of ammonia α_{NH3} was calculated from an equation 1.

Eq. [1]
$$\alpha_{NH3} = \frac{X_{H_2} F^o - F^o_{H_2}}{F^o_{NH3}(1.5 - X_{H_2})}$$

Where: F^0 – total gaseous reactants flow at the reactor inlet, $mol \cdot s^{-1}$, F^0_{H2} and F^0_{NH3} – hydrogen and ammonia flows at the reactor inlet, $mol \cdot s^{-1}$, X_{H2} – molar concentration of hydrogen in the reactor, $mol \cdot mol^{-1}$.

On the basis of degree of ammonia decomposition under given conditions of temperature and ammonia flow rate at the reactor inlet the rate of the ammonia decomposition reaction, related to mass of catalyst, was calculated from an equation 2.

Eq. [2]
$$r_{decomp} = \alpha_{NH3} \cdot F^o_{NH3} / m_{cat}$$

Where: a_{NH3}-degree of ammonia decomposition, F^0_{NH3} - ammonia flow in the reactor inlet, $mol \cdot s^{-1}$, m_{cat} - mass of catalyst, g.

Results and Discussion

Chemical composition of the catalyst was determined with an aid of XRF method and was as follows: 1.05wt% Al_2O_3, 1.23wt% CaO, 0.21wt% K_2O, 4.8wt% Co_3O_4. The rest was composed of iron oxide Fe_3O_4. As a result of potassium hydroxide impregnation two additional catalysts were prepared with potassium oxide content of 0.47wt.% i 0.87wt.% respectively. In that way three catalysts varying one another of potassium oxide content, what was included into the catalyst names FeCo(0.21), FeCo(0.47), FeCo(0.87), were prepared.
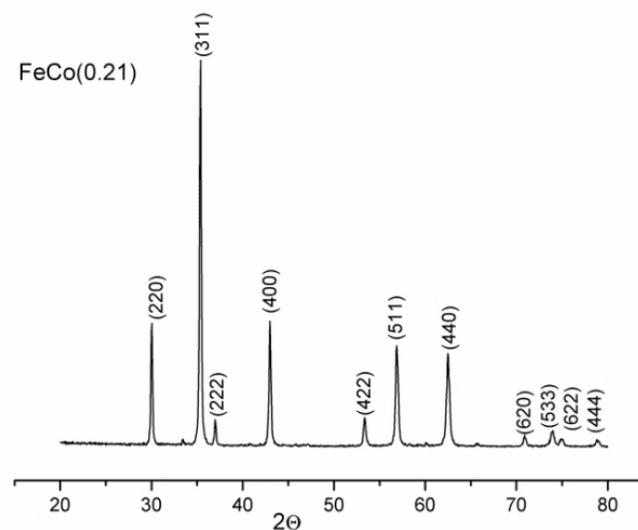
Figure 1. X-ray pattern of the oxidized form of the FeCo(0.21) catalyst.

Results and Discussion

Table 1. Specific surface area of the catalysts in the reduced form and volume of absorbed hydrogen in the TPD-H_2 process.

Catalyst	S_{BET} [m^2/g_{cat}]	V_{H2} [cm^3/g_{cat}]
FeCo(0.21)	10.50	0.3085
FeCo(0.47)	11.28	0.3111
FeCo(0.87)	12.49	0.3154

Results and Discussion
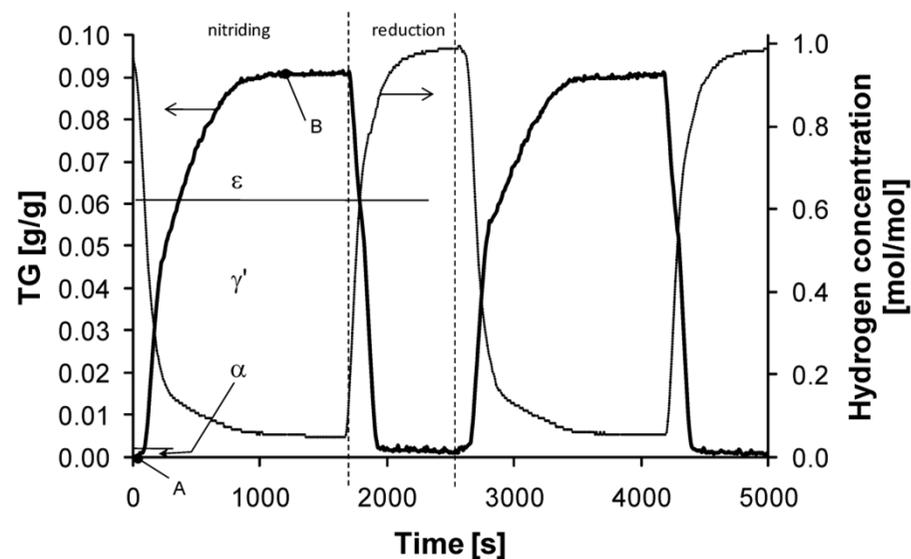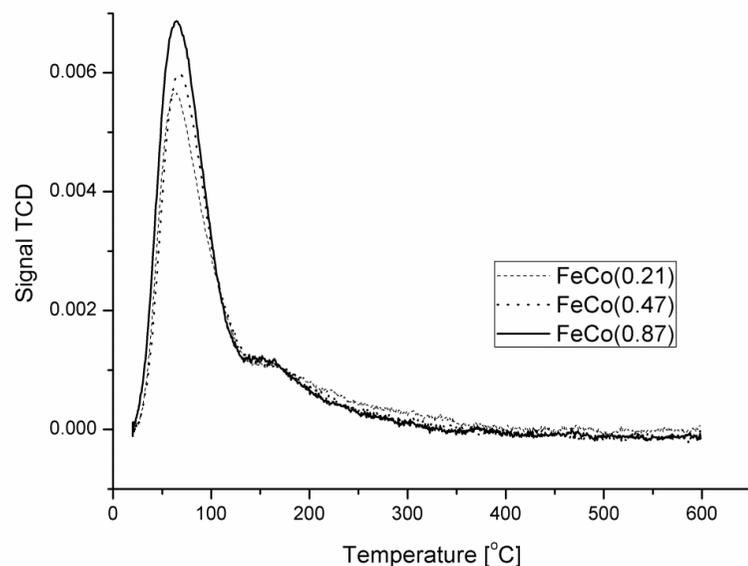
Figure 2. Changes of katharometer signal, connected with changes of hydrogen content and temperature for catalysts with various content of potassium oxide.

Figure 3. Thermogravimetric curve and changes of hydrogen content determined for nitriding process of the alloy FeCo(0.21) catalyst (ammonia content at the reactor inlet - 100%, temperature - 400°C)

Results and Discussion
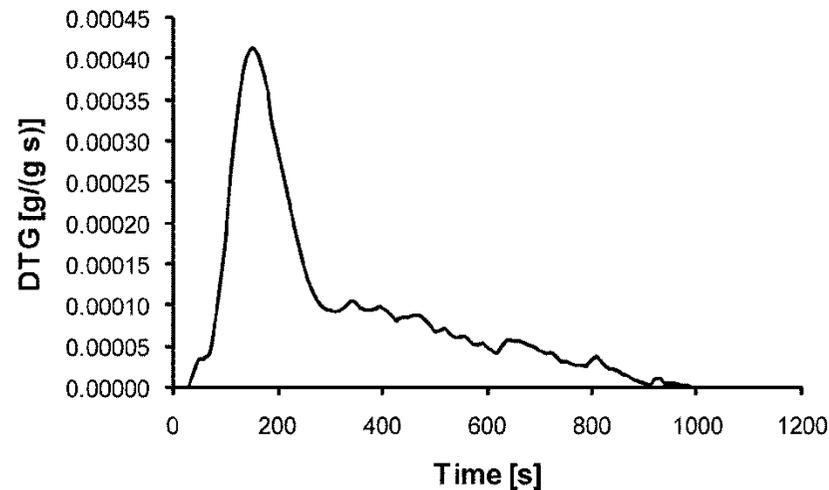
Figure 4. Nitriding reaction rate (ammonia content at the reactor inlet -100%, temperature - 400°C).
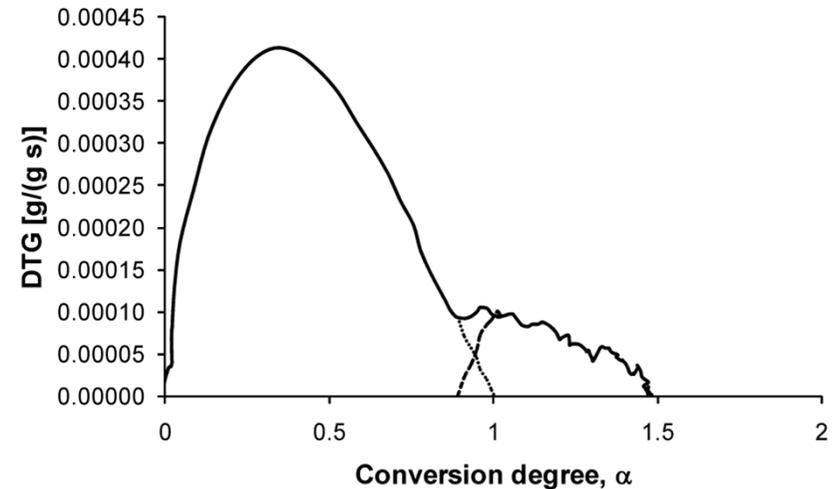
Figure 5. Rate of nitriding reactions of α-FeCo into γ' phase and γ' phase into ε phase.

Results and Discussion
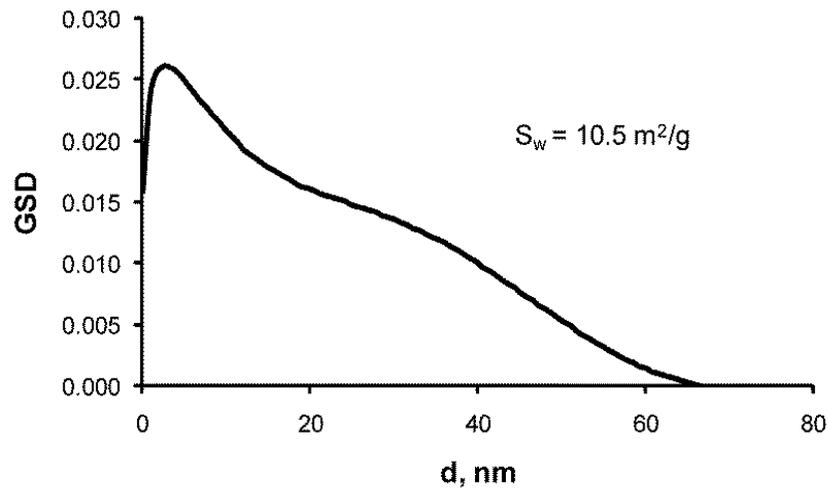
Figure 6. Distribution of nanocrystallites size of the FeCo.
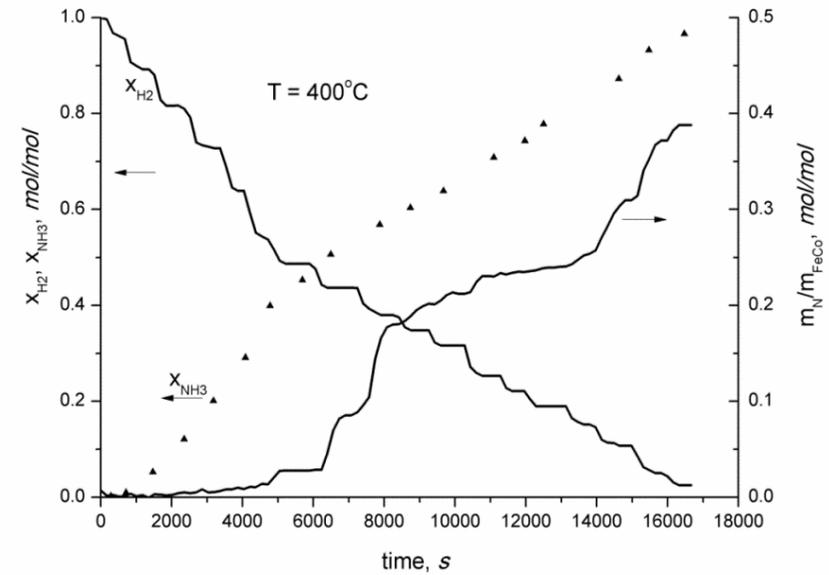
Figure 7. Hydrogen concentration changes and the nitriding degree vs. Time at temperature 400°C.

Results and Discussion
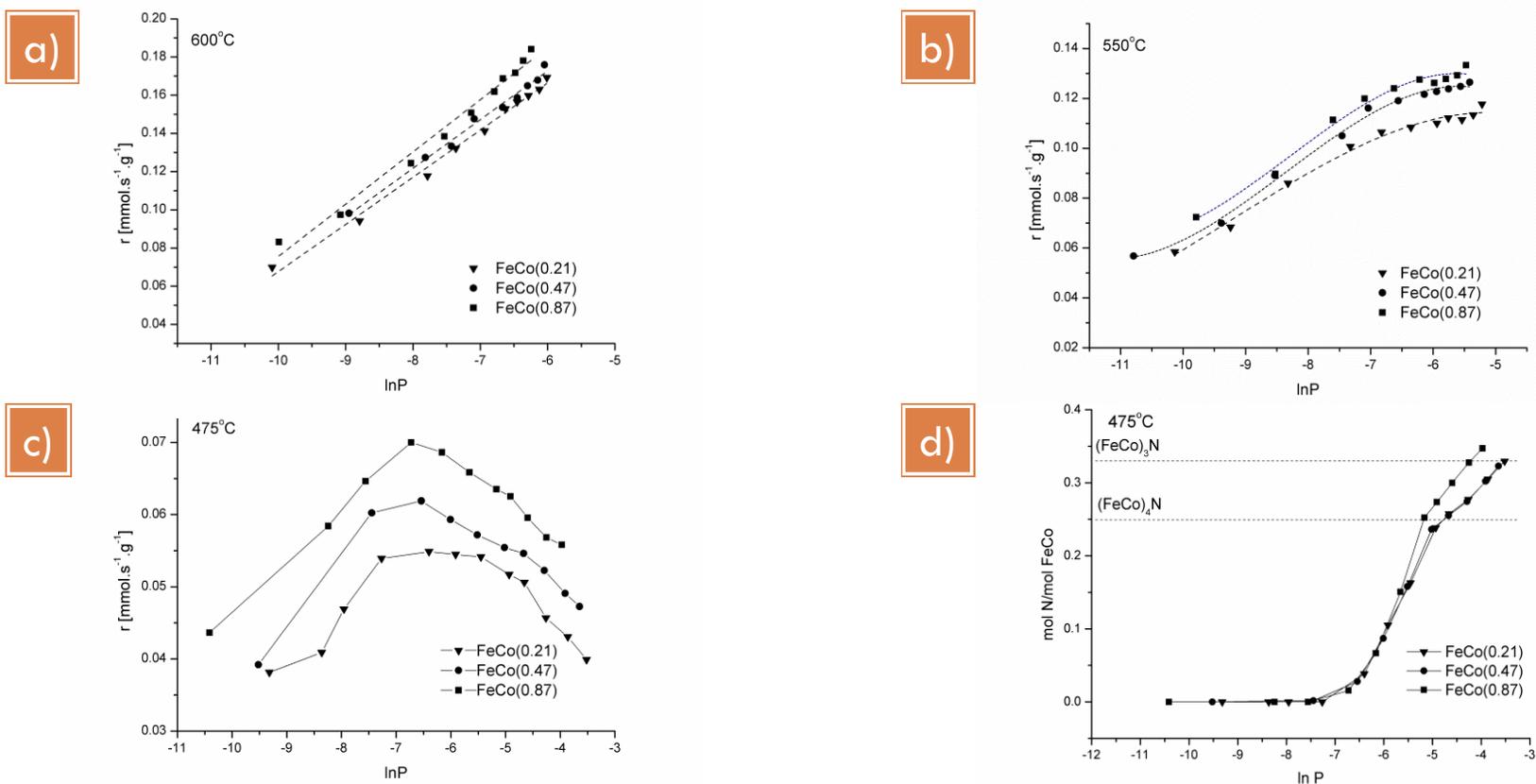
Figure 8. Dependence of the ammonia decomposition rate as a function of nitriding potential (lnP=$p_{NH3}/p_{H2}^{1.5}$) for the catalyst with a low content of potassium oxide: a) at 600°C, b) at 550°C, c) at 475°C, d) mass changes of the catalysts during the ammonia decomposition process at 475°C as a function of the logarithm of the nitriding potential.

Results and Discussion
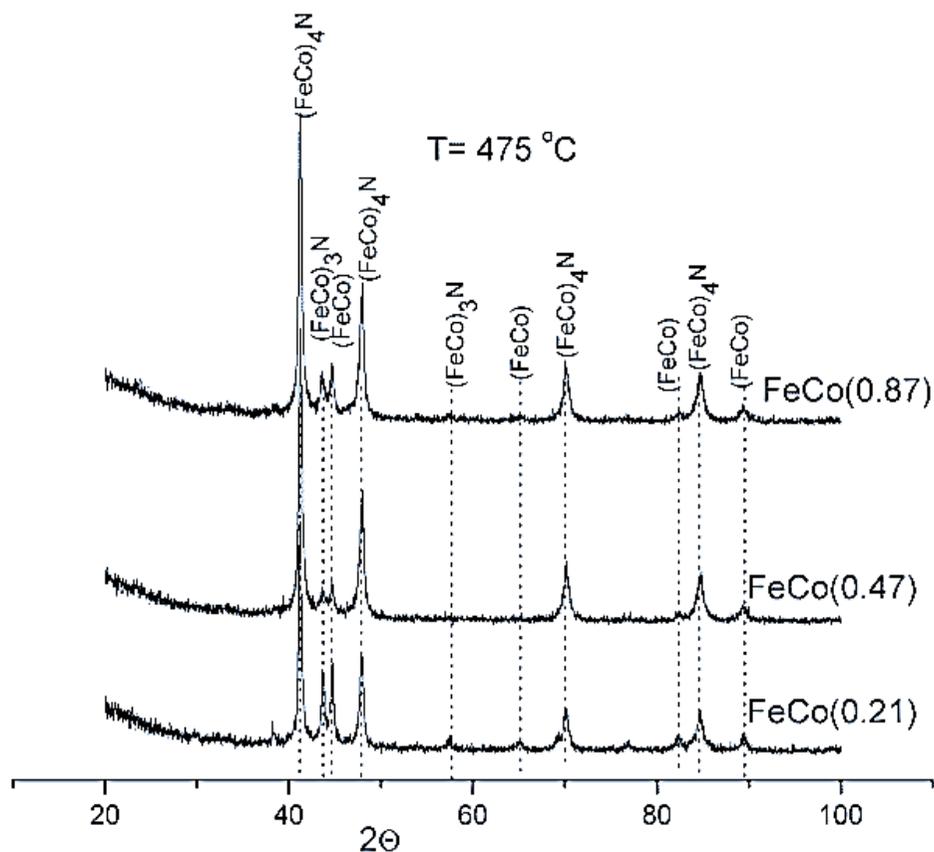
Figure 9. XRD patterns of the catalysts after ammonia decomposition at *475°C.*

Conclusions

Potassium oxide develops specific surface area of the catalyst and increases a number of adsorption sites for hydrogen. An increase in potassium oxide content enhances catalyst activity in the ammonia decomposition reaction. At the temperature of 475°C a process of nitriding of the catalyst takes place, a new phase is being formed, over which the ammonia decomposition rate decreases.