CATALYTIC PROPERTIES OF HYBRID ALUMINA-Pt FILMS PRODUCED ON FeCrAl STEEL IN A COMPARISON TEST ON 2-METHYLOL-3BUTYN-2-OL CONVERSION AND OXIDATION OF CYCLOHEXANE

Kazimierz Reszka*, Jan Rakoczy**, Maciej Lisowski***

*Koszalin University of Technology
Institute of Mechatronics, Nanotechnology and Vacuum Technique
Racławicka15-17, 75-620 Koszalin, Poland
tel/fax: +48 94 3478344
e-mail: kazimierz.reszka@tu.koszalin.pl

**Technical University of Kraków
Department of Organic Chemistry and Technology
Warszawska 2, 31-422 Kraków, Poland
tel.:+48 12 6282116, fax:+48 12 6282037
e-mail: jrakoczy@usk.pk.edu.pl

***University of Technology
Department of Materials Engineering
Racławicka 15-17, 75-620 Koszalin, Poland
tel/fax: +48 94 3478344

Abstract

The higher thermal resistance and the mechanical strength of the catalytic element carriers produced on metal substrates contribute to the further interest of the automotive industry on them despite that they show a smaller development of the surface compared to the ceramic carriers. The present work was focused on testing the catalytic properties of oxide films obtained as a result of the high-temperature oxidation of 0H18J5 steel foil under mixture of oxygen and argon which were coated with platinum by reactive dc magnetron sputtering. Hybrid coatings obtained by the oxidation of metal foil prior coated with aluminum nanofilms and then with platinum and the aluminum- platinum composites were also tested. The catalytic activity of the obtained coatings was tested by the pulse method in 2-methylol-3-butyn-2-ol decomposition reaction and the flow method in the process of cyclohexane oxidation. A catalytic test enabling the parameters of cyclohexane oxidation (temperature, time of reaction, cyclohexane concentration in zone of reaction) using the air to be controlled was developed for this flow method. The tests being carried out revealed an influence of different configuration of oxide films and platinum on their catalytic properties. Moreover, a high activity of alumina-Pt systems in the process of cyclohexane reheating with the air was confirmed.

Keywords:

1. Introduction

The current progress in research work and technology of catalysts has contributed to their established position in chemical, petrochemical, pharmaceutical and automotive industries. The intensive development of new research techniques on a molecular level and on a nanometric scale is conductive to the implementation of programs for the more and more intensive introduction of catalytic technology to the power, the biotechnological, the metals producing industry and the environmental protection. It especially applies to the opportunity of limiting the energy and saving the raw materials, and also the unification of catalysts.

The experimental investigations generally decisive in the suitability of catalysts one may divide into three fundamental areas of:
1. the chemical composition and the structure, which include strength tests as well,
2. the surface development and its chemical activity with identification of active sites,
3. the specificity of catalyst and the deactivation capacity.

These investigations were carried out using the most recent techniques [1] as follows:
- *scanning electron microscopy and X-ray microanalysis,*
- *transmission electron microscopy and electron diffraction,*
- *X-ray diffraction for phase composition analysis and crystallite size (powder method),*
- *X-ray photoelectron spectroscopy (XPS),*
- *IR spectroscopy,*
- *Raman spectroscopy,*
- *Mössbauer spectroscopy,*
- *cryosorption methods (BET),*
- *strength tests*:
- and *catalytic tests including chromatographic analysis and mass spectroscopy:* which allows the identification of products, the rate of catalytic reactions, the degree of substrate treatment, the catalyst efficiency and the selectivity to be tested.

The rate of catalysed reaction, which depends on temperature, pressure and concentration of substrate components, is one yardstick of the catalyst activity. This rate also depends on the time of reaction following from changes in reagents concentration affected by the course of reaction. [2, 3].

The ratio of the reaction rate A to the mass m_k or the catalyst volume v_k, or its specific surface is defined as *the specific reaction rate r*.

$$r = \frac{A}{m_k} = \frac{A}{v_k} = \frac{A}{S_k}. \tag{1}$$

The conversion x, which expresses the ratio of the amount of treated substrate n_{su} to the total amount of substrate subjected to reaction n_{os}, i.e. the degree of substrate treatment, is often applied as a measure of the activity:

$$x = \frac{n_{su}}{n_{os}} = \frac{\Sigma n_{su,i}}{n_{os}}, \tag{2}$$

where:

$n_{su,i}$ = an amount of the product (i) obtained from the treated substrate n_{os}

An amount of the product (i) related to the substrate is defined as the product output y_i

$$y_i = \frac{n_{su,i}}{n_{os}}. \tag{3}$$

2. Experimental procedure

A pack in the form of a roll composed of 4 corrugated foil strips separated by 4 flat foil strips 35x35 in dimension were used for testing the catalytic activity of laminar systems made on the basis of FeCrAl steel foil d=0.05 mm in thickness, using:
- the pulse test for which 2-methyl-3-butyn-2-ol was used as a probe molecule,
- the flow test designed for the process of cyclohexane oxidation consisted in supplying the reactor with reagent at a steady flow rate.

Specimens specified in Table 1 subjected to testing were marked in this way that the uncoated foil has an "r" symbol, the foil modified by additional coating with a nanofilm – "Al" or "Pt"

element symbols, and the specimens modified by oxidation – an "ox" symbol.

Tab. 1. Tabulation of specimens subjected to catalytic tests under oxidation conditions; temperature 860⁰C, time 24 h, argon flow rate 1200 ccm/h, O₂ flow rate 2400ccm/h

No.	Oxidation	Layer composition	Test symbol
1	-	-	r
2	-	Al	r+Al
3	-	Pt	r+Pt
4	-	Al + Pt (composite)	r+(Al+Pt)
5	+	-	rox
6	+	Al	(r+Al)ox
7	+	Pt	(r+Pt)ox
8	+	Al + Pt (composite)	[r+(Al+Pt]ox

Strongly unsaturated alcohol which at basic sites was decomposed into acetylene or acetone (reaction r_b), whereas at acidic sites it was dehydrated into 2-methyl-3-butyn-2-ol ,"byn" in short, (reaction r_a) was subjected to the pulse test, Fig. 1.

Fig. 1. Reaction network of 2-methyl-3-butyn-2-ol decomposition

This method allows the type and the activity of catalytic sites distributed on the surface of tested specimens to be easily characterized. A sample result obtained by the chromatographic analysis of the reaction products is presented in Fig.2. The composition of 2-methyl-3-butyn-2-ol conversion products was determined using the calibration coefficients, which allow the surface of chromatographic peaks to be recalculated into mass fractions of individual compounds in the post-reaction mixture.

Fig. 2. Sample chromatograph of 2-methyl-3-butyn-2-ol catalytic conversion products on (r+Pt)ox hybrid laminar system

The oxidation reaction of $C_6 H_{12}$ hydrocarbon, i.e. cyclohexane was used for the flow test. The reactor was supplied with the air saturated with cyclohexane vapours and the activity of foils obtained in the reaction of oxidation was tested.

$$mC_6 H_{12} + 9nO_2 = 6nCO_2 + 6nH_2O + (m-n)C_6 H_{12}.$$
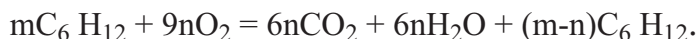
As a criterion of the catalyst activity at a given temperature the quantity of conversion computed from the difference of cyclohexane vapour concentration in the gas supplied to the reactor and in the post-reaction products was assumed.
The conversion was calculated according to the following relation:

$$x = \left(\frac{\overline{S}_{wc} - \overline{S}_{kc}}{\overline{S}_{wc}} \right) 100\%, \tag{4}$$

where:

$\overline{S}_{wc}$ = average surface of a cyclohexane peak obtained by the substrate analysis,

$\overline{S}_{kc}$ = average surface of a cyclohexane peak on a chromatogram of the product.

Figure 3 shows sample chromatogram specimens.
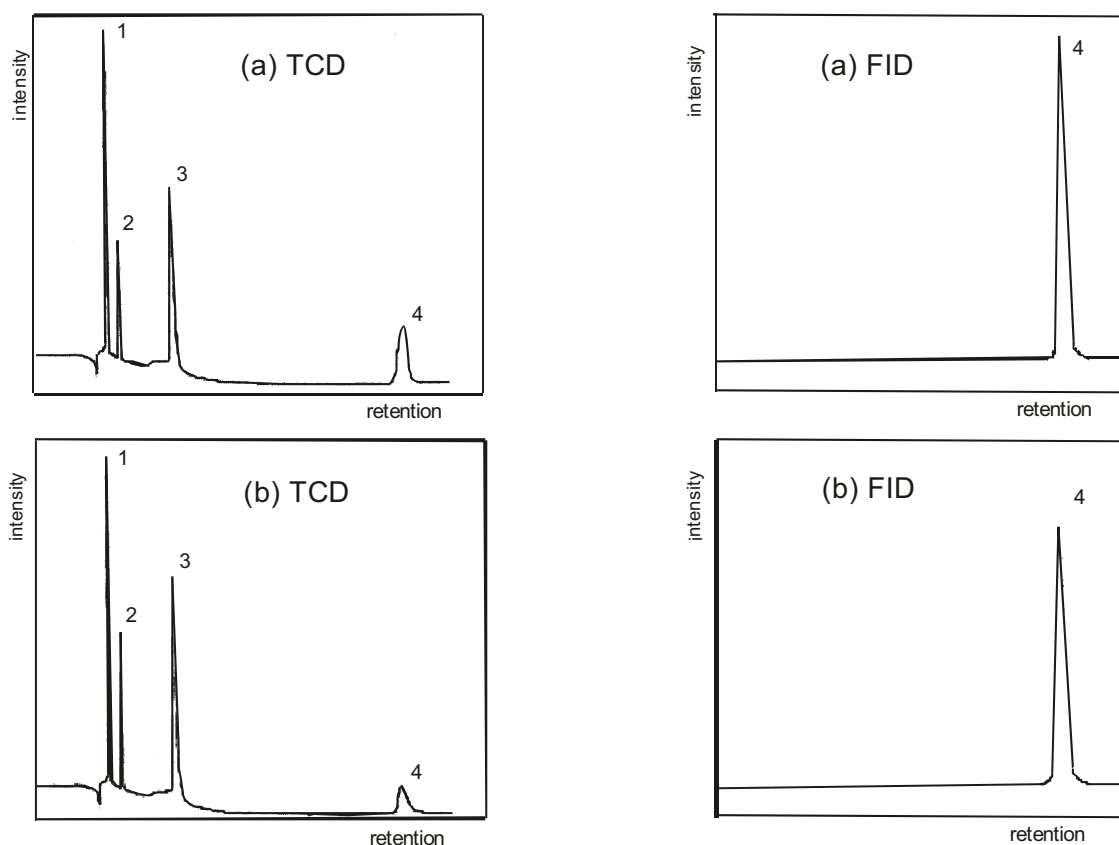
Fig. 3. An example of cyclohexane chromatograms after reheating in the presence of catalysts, at two temperatures (a) 300^0C and (b) 450^0C (a)TCD/FID - area%: 1- air 51,80, 2- CO$_2$ 3,84, 3- H$_2$O... 15,39, 4- c-sane... 12,91; (b)TCD/FID – area% :1- air 54,99, 2- CO$_2$ 7,43, 3- H$_2$O…… 26,45, 4- c-sane… 10,46

The catalytic tests were carried out on an experimental setup that was used for the pulse tests at the participation of 2-methyl-3-butyn-2-ol [4, 5] which included the reactor connected „on line" with a gas chromatograph of a SRI 8610C type (Fig. 4) equipped with two detectors (FID and TCD). An analysis of the products of reaction was carried out using a column filled with the Q poropack.

An electric power system of the reactor made it possible for the temperatures in the zone of reaction to be controlled within the range 200-450^{0}C, at a point measurement, with an accuracy of +/- 1^{0}C. Respecting the total height of the specimen (70mm), the stability and the minimising of the temperature gradient in the zone, where the specimen was place, played a significance part in catalytic tests. An emission spectral pattern of the reactor chamber recorded with a thermovision camera is illustrated in Fig. 5.
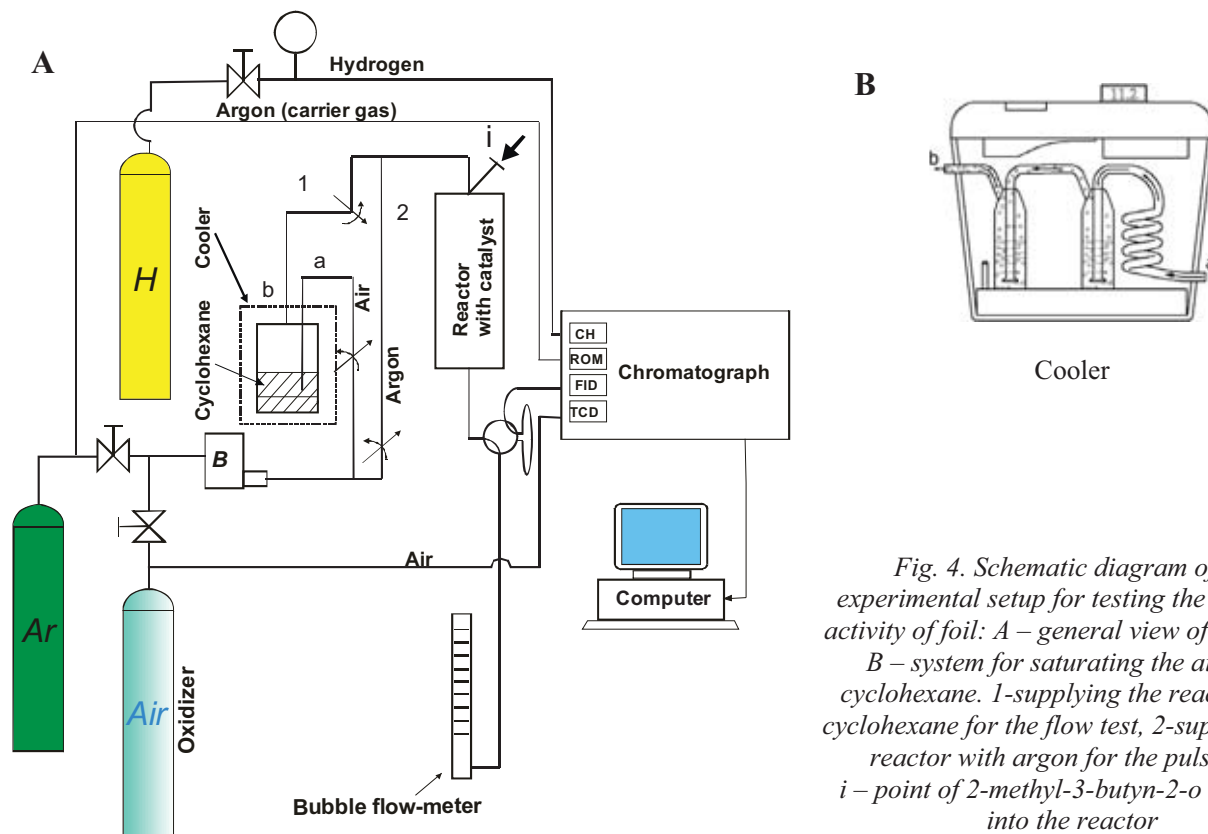
Fig. 4. Schematic diagram of an experimental setup for testing the catalytic activity of foil: A – general view of the setup, B – system for saturating the air with cyclohexane. 1-supplying the reactor with cyclohexane for the flow test, 2-supplying the reactor with argon for the pulse test, i – point of 2-methyl-3-butyn-2-o injection into the reactor
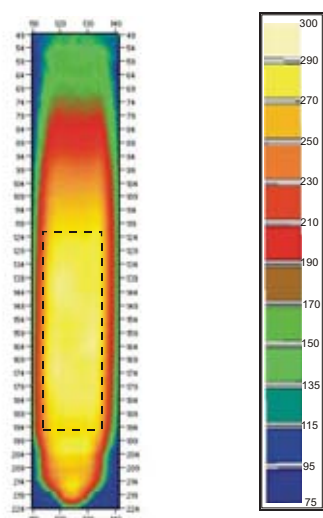
Fig. 5. Thermogram of the reactor chamber with a marked zone where the specimens for catalytic tests were placed

3. Results

In case of the pulse test the accuracy of the temperature control, the rate of a carrier gas flowing through the micro-reactor and the volume of 2-methyl-3-butyn-2-ol injection were the deciding factor on the course of the test reaction. For improving the measuring reliability each measurement was taken twice and the steady program of temperature increase for the reactor from 200 do 350 ^{o}C was applied.

In case of the catalytic tests, where the flow technique was applied, an additional problem was concentration of cyclohexane to be held constant in the air supplied to the reactor. Therefore, after carrying out a series of initial experiments it was decided to make use of the air saturation system with two bubbling washers filled with cyclohexane placed in a thermostat at the temperature 11-12^{0}C through which the air was flowing at the rate of 32ml/min $\pm$ 1.5 ml/min.

The catalytic test for determining the activity of acidic and basic sites in 2-methyl-3-butyn-2-ol conversion (Figs 6-12).

After coating the raw foil (**r**) with an Al film (**r+Al** specimen) there was a significant decrease in the activity of basic sites (Fig. 6) and a slight increase in the catalytic activity (Fig. 7) of acidic sites measured by conversion to 2-methyl-1-butyn-3-yn (B-yn) so, that the catalytic activity of the specimen coated with a metallic Al film was distinctly lower than raw foil. However the specimens coated with a Pt film, i.e. **r+Pt** and **r+(Al+Pt)** revealed the high catalytic activity and the basic sites dominated their surface. The highest activity showed the foil coated with an Al+Pt composite (Fig. 6).
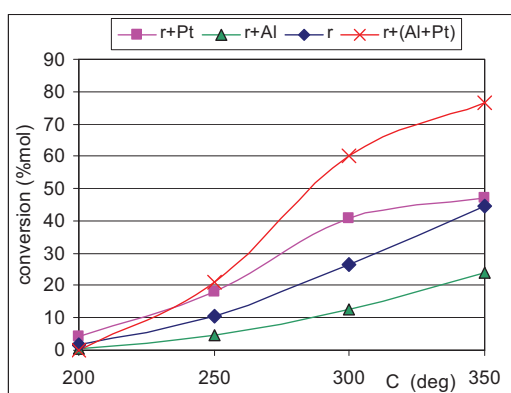
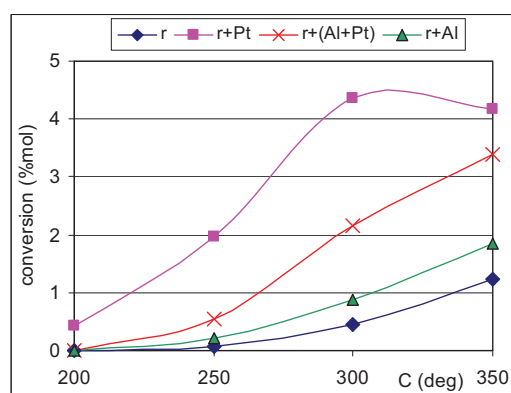Fig. 6. Conversion to acetone for coated foil, not oxidised

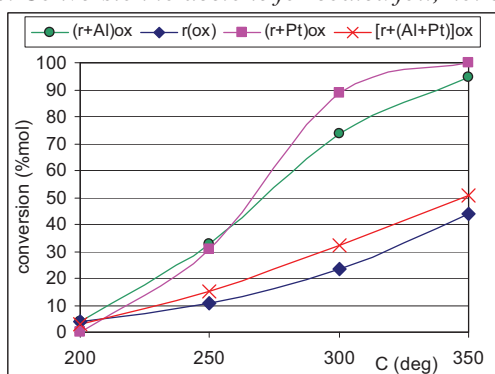Fig. 7. Conversion to byn for coated foil, not oxidised

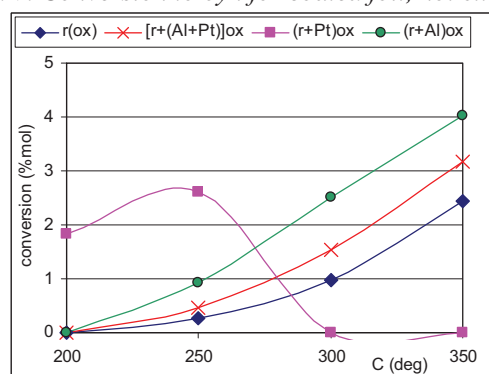Fig. 8. Conversion to acetone for coated foil, oxidised

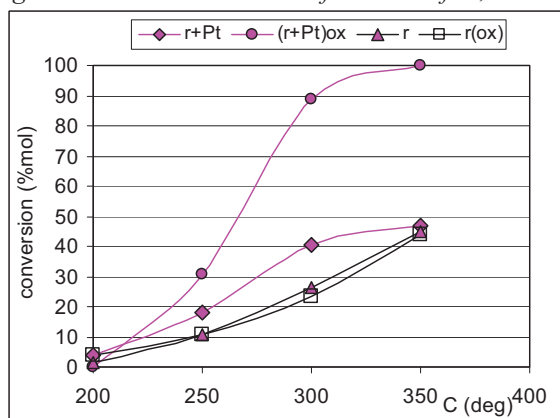Fig. 9. Conversion to byn for coated foil, not oxidised

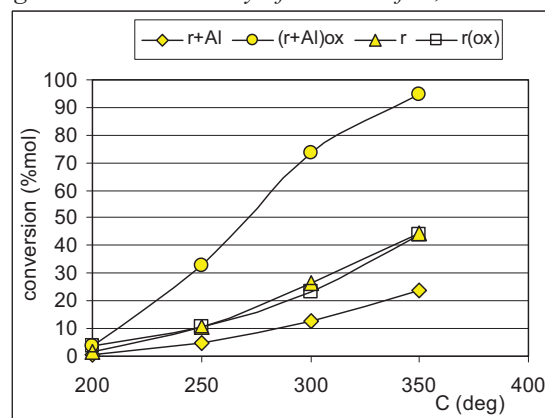Fig. 10. Conversion to acetone for raw foil and coated with Pt

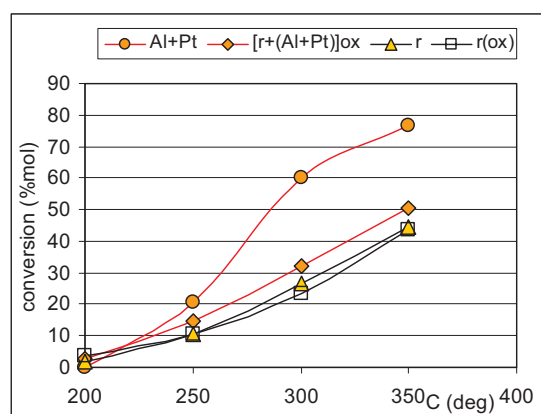Fig. 11. Conversion to acetone for raw foil and coated with Al

Fig. 12. Conversion to acetone for raw foil and coated with Al+Pt composite

The oxidation process, which resulted in forming the Al_2O_3 film on the foil surface, brought out an increase in the catalytic activity retaining the dominant role of basic sites. The highest increase in the activity was observed in case of the **(r+Pt)ox** specimen (Figs 8 and 9).

Due to a small share of the acidic site activity both on the non-oxidised foil and the laminar systems non-oxidised and oxidised, not exceeding 5% conversion of the test substance, the effect of the oxidation process on the development of basic sites was subjected to an analysis. The data presented in Fig. 10 show that the oxidation process of the foil without additional coats has not influenced the activity of its sites despite the formation of a well-developed oxide film [5, 7].

However, an essential increase in catalytic activity (Fig. 11) was affirmed in case of oxidising the foil specimen coated with an Al film. As a matter of fact the layer of metallic aluminium brought about the site interlock of initial foil and the decrease in its activity compared with raw foil (Fig. 6), but a long-lasting process of oxidation (24 hours) caused that the activity of the obtained system increased by 100% in relation to the uncoated foil. This increase was due to the formation of the morphologically and structurally diversified hybrid oxide film from Al contained in the alloy and Al deposited on its surface.

The expected effect of an increase in the activity of initial foil was obtained by coating it with a Pt film. The pulse test results (Fig. 10) revealed that the foil oxidised with a Pt-**(r+Pt)ox** film was marked by the highest activity. If in case of the other specimens being tested the conversion was increasing monotonically as a function of temperature within the range from 200 do 350 ^{o}C, then in case of the oxidized foil with a Pt film the conversion of the order of 100% was already observed at the temperature slightly above 300^{0}C.

Owing to the higher activity of oxide systems obtained at the presence of Al and Pt layers, the experimental investigations on the FeCrAl foil coated with Al+Pt film and the oxidized composite system **[r+(Al+Pt)]ox** (Fig.12) were carried out. They showed a significant similarity of the catalytic activity for both these specimens at lower temperatures not exceeding 250^{0}C and the significant differences in the course of conversion curves above 300^{0}C. It was also affirmed, that the oxide system on the basis of composite showed a slightly lower catalytic activity than the oxide systems on the basis of Al and Pt (Figs 10 and 11). It was likely caused on one hand by the inhibition of the oxide crystallite growth by Pt, and on the other hand by masking Pt by growing crystallites and "pushing it deep in the layer". This phenomenon was examined during the earlier investigations [8, 9].

The catalytic test of the activity of the systems obtained in the process of cyclohexane reheating, Figs 13-16

Due to coating the metallic nanofilm (Pt and Al) on FeCrAl initial foil, the catalytic activity in the process of cyclohexane reheating (Figs 13, 14 and 15) was increasing. In case of coating the foil with an Al film, only a slight increase in the conversion for a **r+Al.** system compared with the conversion of cyclohexane on **r** raw foil was observed. Its catalytic activity within the test range of temperatures (Fig. 14) was growing linearly along with an increase in the temperature of the

oxidation process. Coating the foil with a Pt film (Fig. 15) contributed to a high increase in the catalytic activity at the temperatures above 450^0C.

The oxidation process of the initial foil and the system coated with Pt or Al films caused the activity in the reaction of reheating to be increased. A (r+Pt)ox specimen, for which already at the temperature of 300^0C (Fig.15) a degree of cyclohexane conversion was observed at the level above 30%, revealed the highest activity.

Due to coating the foil with (Al+Pt) composite the obtained system was marked by somewhat better catalytic properties compared with an **r+Al** system, but its activity was considerably lower than in case of systems coated with **r+Pt** i **(r+Pt)ox** metallic platinum films. As a matter of fact, the composite oxidation (Fig. 16) contributed to an increase in the cyclohexane conversion in the reaction of reheating, but its activity was by half lower compared with a **(r+Pt)ox** system.

The obtained results were in a good agreement with the conclusions drawn from the pulse tests in reference to the partial locking (by an Al_2O_3 film formed during the composite oxidation) the access of reacting particles to the active sites situated on the surface of Pt crystallites.
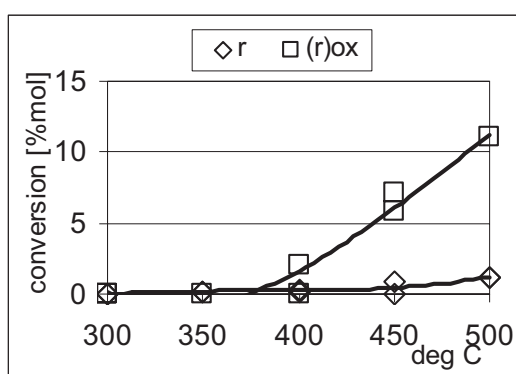

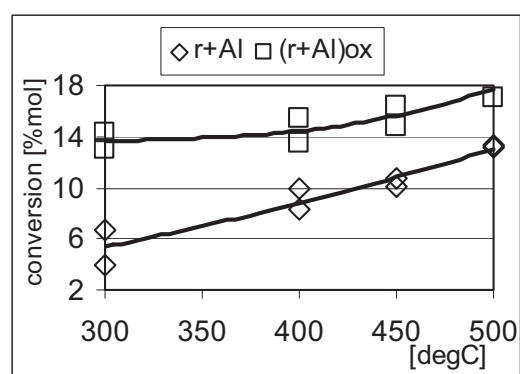Fig. 13. Cyclohexane conversion on raw foil

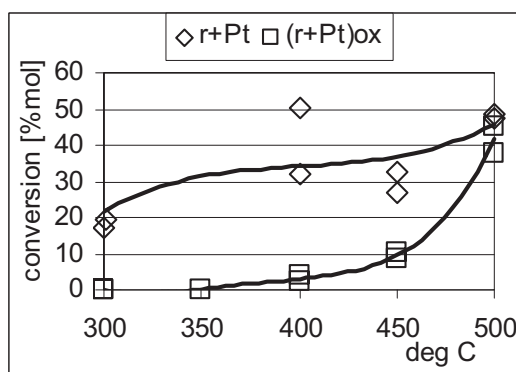Fig. 14. Cyclohexane conversion on foil with an Al nanofilm

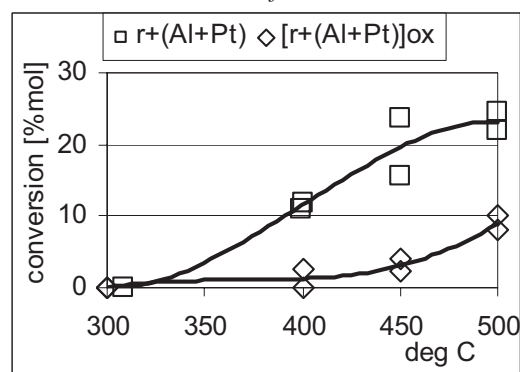Fig. 15. Cyclohexane conversion on foil with a Pt nanofilm

Fig. 16. Cyclohexane conversion on foil with a nanofilm of Al+Pt composite

4. Conclusions

1. The deposition of the metallic platinum nanofilm on FeCrAl foil using one of PVD techniques and the oxidation process for nanolaminar systems of Al or Pt under the mixture of oxygen and argon, [10] caused the catalytic activity to be increased due to an increase in the surface development.

2. Among the laminar systems being tested the foil coated with Pt and then oxidised revealed the highest activity in the processes of 2-methyl-3-butyn-2-ol conversion and cyclohexane reheating.

3. The laminar systems produced by the method of oxidising the Al+Pt composite nanofilm are marked by relatively worse catalytic properties, which was caused by masking the Pt phase with the oxide phase.

References

[1] Najbar, M. (red), *Fizykochemiczne metody badań katalizatorów kontaktowych,* W. Uniw. Jagiell. Wyd.1, Kraków, 2000.

[2] Sarbak, Z., *Kataliza w ochronie środowiska,* W. N. UAM Poznań, 2004.

[3] Ziołek, M., Nowak, I., *Kataliza heterogeniczna,* W.N.UAM Poznań, 1999.

[4] *Badania właściwości katalitycznych i strukturalnych hybrydowych wielowarstwowych układów na podłożach ze stali FeCrAl,* Sprawozdanie z tematu PB-0819/T08/2002/22, 2004.

[5] Reszka, K., *Structure and Catalytic Testing of Hybrid Al$_2$O$_3$ Systems Deposited on Heat Resisting Steel Substrate by High-Temperature Oxidation and PVD Methods,* Advances in Science Technology, 45 pp. 2110-2117, 2006.

[6] Reszka, K., Rakoczy, J., Morgiel, J., *Deposition of Thin-Film Hybrid Systems on FeCrAl-Steel Substrate and Testing Their Catalytic Properties*, Journal of. KONES International. Combustion Engines, vol.12, 3-4, pp. 211- 218, 2005.

[7] Reszka, K., Rakoczy, J., Murzyński, D., Homa, M., *Strukturalne badania mikroskopowe i katalityczne warstw albuminy, uzyskanych na stali Fe18Cr5Al w wyniku jej wysokotemperaturowego utleniania,* Materiały XXXIX Ogólnopolskiego Kolokwium Katalitycznego, s. 336-339, 2007.

[8] Reszka, K., Morgiel, J., Reszka, J., *Structure and properties of an alumina/amorphous-alumina/platinum catalytic system deposited na FeCrAl steel,* Journal of Microscopy., vol. 224, 1 pp. 46-48, 2006.

[9] Reszka, K., *Nanocomposites alumina/Pt produced by PVD and thermal oxidation methods used in catalytic applications,* Vacuum., 81, pp 1202 – 1206, 2007.