CATALYSTS FOR HYDROGEN REMOVAL: KINETIC PARADOX AND FUNCTIONING AT HIGH CONCENTRATION OF HYDROGEN

Shepelin V.¹, Koshmanov D.², Chepelin E.³

CJSC ISP Company "Russian Energy Technologies"

¹CJSC ISP "RET" Staroobrjadcheskaya str., 46A, Moscow, 111024, Russia, vladshep@hotmail.com
 ²CJSC ISP "RET" Staroobrjadcheskaya str., 46A, Moscow, 111024, Russia, ret@retech.ru
 ³CJSC ISP "RET" Staroobrjadcheskaya str., 46A, Moscow, 111024, Russia, ret@retech.ru

ABSTRACT

Platinum metals dispersed on a porous carrier, e.g. γ -Al₂O₃, are used as catalysts for removal of small amounts of hydrogen from the air, where the excess of oxygen is significant.

The recombination reaction of H_2 and O_2 on smooth platinum proceeds at a high rate only in gas mixes with an excess of hydrogen. When the concentration of oxygen exceeds that of hydrogen, in terms of stoichiometric ratio, the process slows down sharply and eventually stops completely.

In research undertaken at the Karpov Institute of Physical Chemistry (Moscow) forty years ago the electrochemical mechanism of red-ox reactions was proposed as an explanation for this inhibition by excess oxygen. The results of ellipsometric analysis pointed to the formation of a protective monolayer of PtO molecules on the Pt surface in an oxygen-rich atmosphere. It was observed that the recombination reaction proceeds at a high rate with the use of a porous catalyst at any concentrations of reactant gases. The reason for that lies in the mechanism of the catalysis: the reaction proceeds at a certain depth in the porous body of the catalyst. Hydrogen, which has higher mobility, penetrates in larger quantity than oxygen, thus creating there the stoichiometric excess.

To test the proposed mechanism of recombination, the catalytic reaction was studied a) with porous carriers of various thicknesses and b) with metal grids of various porosities covering the catalyst. The data obtained have confirmed unequivocally the earlier hypothesis of hydrogenation of a porous catalyst.

Such insight has allowed the authors to develop more effective prototypes of catalyst for removal of hydrogen. In particular, by using a porous grid cover to remove excess heat in the reaction zone of the catalyst plate we achieved a considerable expansion of the region of hydrogen concentrations where the catalyst is both effective and reliable.

1. INTRODUCTION

One of the most researched reactions of inorganic chemistry, recombination of hydrogen and oxygen on the surface of a catalyst, still remains mysterious. For much of the time since the second half of the 18th century, when Antoine Laurent de Lavoisier and Henry Cavendish first observed the formation of water [1], this reaction has been an object of purely academic research. Only in the last 30 years has hydrogen-oxygen recombination received wide practical interest because of, on the one hand, the growing interest in hydrogen as a potential 'ecological' fuel, and, on the other, the extreme hazard it presents.

Among the means to prevent destructive explosions by removing hydrogen from various enclosed spaces (e.g. warehouses for hydrogen storage, fuel element zones, hydrogen refueling stations, generator workshops in electric power stations, where hydrogen is used as a coolant, and water-cooling circuits of nuclear power stations during normal and catastrophic failure conditions) the catalytic method for hydrogen removal has been widely applied thanks to the simplicity and reliability of devices based on it.

In this article we describe catalysts which are used in devices capable to function in a passive regime, due to thermal gas convection and exchange with the environment. The catalytic method for hydrogen removal has received widest application in hydrogen safety systems of nuclear power plants with water-cooled reactors. The first passive autocatalytic recombiners (PAR) appeared in the 1980s.

The design of PAR is simple: it consists of a vertical metal pipe, normally rectangular in its section, 1-1.5 meters high, with the catalytic cartridge at its lower part. When hydrogen and oxygen contact the catalyst the exothermic reaction begins

$$2H_2 + O_2 \rightarrow 2H_2O (gas) + 244.9 \text{ kJ/mole}$$
 (1)

This causes thermal convection which creates the conditions for continuous operation of PAR and removal of hydrogen from the surrounding environment. Of the wide variety of catalysts for the oxidation of hydrogen, platinum and other metals of the Pt-group are used most often. In such devices dispersed metal-catalyst is distributed in a porous matrix (e.g. oxides of metals, ceramics, silicagel, graphite). The dispersion of metal both reduces cost and creates a large surface area where gases can react. The porous matrix can either be used itself as a carrier of the catalyst [2] or be put as a coat on another carrier, e.g. a stainless steel plate [3, 4]. Pt is known to be an effective catalyst at almost any concentrations of reactants. However, at concentrations of hydrogen between 8 and 90 % v/v some measures are necessary in order to prevent overheating of the catalyst and ignition of hydrogen (at 500-600^oC). At these concentrations of hydrogen the temperature of the catalyst has to be maintained by thermostatic cooling [5]. Devices with a porous catalyst are normally used for removing relatively small amounts of hydrogen from the airspace of premises. For example, PAR produced by Framatome ANP (Siemens) for nuclear power stations can function in hydrogen concentrations of 2-8% v/v (in dry air) and 2-14 % v/v (at steam concentrations up to 72 % v/v) [6]. Notably, these are conditions with a large stoichiometric excess of oxygen.

2. KINETICS OF CATALYSIS IN ENVIRONMENTS WITH EXCESSES OF HYDROGEN AND OXYGEN

By using the method of "temperature gradient" it was observed [5] that hydrogen-oxygen recombination on smooth platinum, in remarkable contrast to the porous catalyst, proceeds much more slowly when there is an excess of oxygen in the environment than when there is an excess of hydrogen. At a tenfold excess of oxygen over hydrogen the rate of reaction falls to zero. Some 40-50 years ago this phenomenon of 'oxygen inhibition' was researched by many scientists. One of the authors of this paper with his colleagues at the Karpov Research Institute (Moscow) found a similarity in the kinetics of catalytic processes for Pt and the whole range of metals of Pt-group (Pt, Pd, Ir, Rh and Ru) in a gas phase and in water solutions [7]. It was shown voltammetrically that the electrode potential of platinum reflects the ratio of concentrations of H_2 and O_2 in both systems. On this basis the authors concluded that partial reactions of O_2 reduction and H_2 oxidation in both systems proceed independently of each other, being connected only by a transfer of electrons through the metal-catalyst, i.e. that the mechanism of catalysis could be described in terms of electrochemistry.

Later, the reason for 'oxygen inhibition' was established using ellipsometry, a research method for thin films on a smooth surface [8]. It appeared that a monolayer of PtO was forming on the Pt surface during both the catalysis and electrode process. This fact led to the question why the highly porous Pt-catalyst does not exhibit the inhibition effect under the same condition of O_2 excess. To understand the reason for such a kinetic paradox, the behavior of catalysts with different porosity and thickness of active layers was studied. As a model system, Pt plates (6x8 cm in size) were used. The plates were covered with porous, sponge-like Pt by depositing it electrochemically from a solution of H₂PtCI₆. Samples of catalyst with deposits of various thickness were tested in an air environment containing 4 % v/v H₂, (H₂/O₂ mole ratio 0.16).



Figure 1. Microphotographs of catalysts with smooth Pt (No.1) and Pt(porous)/Pt deposits with thickness 0.025 mm (No.2) and 0.27 mm (No.3) and voltammetric curves for No.2 and No.3.

The photos from Fig.1 show the surface of three samples, smooth platinum (No.1) and two porous deposits of thickness 0.025 mm (No.2) and 0.27 mm (No.3). The increasingly rough surface is clearly visible. It was found on testing these samples that only No.3 was an active catalyst. The rate of the reaction (for 1 cm² of catalyst plate) was 7.25 ml/min with the catalyst temperature rising to 320° C. In order to study the characteristics of porous structures of Pt/Pt deposits the electrochemical methods of Coulomb-metry and linear-sweep voltammetry were used. In the lower part of Fig.1 only two curves for samples No.2 and No.3 are presented because currents for sample No.1 (smooth Pt) were too small to display. The measurements were conducted in a three-electrode cell in 1N H₂SO₄ at potentials for hydrogen and oxygen chemisorption ranging from -0.2 to +1.2 V vs. Ag/AgCl as a reference electrode

with a potential change rate of 50 mV/s. The active surface areas of catalysts were calculated on the basis of the electrical charge of oxygen and hydrogen chemisorption on Pt, according to [9].

	No.1	No.2	No.3
Electrical charge per	0.60	1.81	8.33
1 cm ² of geometric			
surface, mC			
Roughness degree (ratio	1.5	4,5	20,9
of active Pt/Pt surface			
area to geometric one)			
Thickness of Pt deposit,	0	0.025	0.27
mm			
Weight of Pt deposit on	0	0.0069	0.0670
1 cm^2 of geometric			
surface, g			
Specific surface of Pt	0	0.065	0.031
deposit, m ² /g			
Catalytic activity	No	No	Yes

Table 1. Characteristics of samples of catalysts from Fig.1 calculated from the results of Coulomb-metry and voltammetry.

Table 1 presents various characteristics of samples of catalysts calculated from voltammetric curves. The catalytically active sample (No.3) had a thickness of porous Pt deposit of 0.27 mm with a specific surface area of $0.031 \text{ m}^2/\text{g}$.

The results of these experiments explicitly demonstrated that the catalytic reaction accelerates with the increase in thickness and weight of Pt/Pt deposit but without any significant change in specific surface area. This fact led the authors to conclude that the catalytic reaction proceeds at some depth in the porous layer. It was suggested that at such a depth in the porous Pt deposit, where the size of pores restricts the diffusion of gas molecules and the process is determined by collision with walls, the conditions for Knudsen diffusion are realized. Because the diffusion coefficients for hydrogen and oxygen differ more than 3.5 times (under normal conditions), a gradual enrichment in hydrogen in the depth of the Pt deposit takes place. As a result, even with a low concentration of H₂ in the surrounding environment (4 % v/v), at a thickness of Pt deposit somewhere between 0.025-0.27 mm, as follows from the data of Tab.1, the H₂/O₂ mole ratio in the depth of the catalytic layer becomes more than 2. This allows the catalytic reaction to proceed.

This hypothesis suggests that only the catalysts with a sufficient thickness of porous layer will be active in an atmosphere with an excess of oxygen over hydrogen. It also leads to the conclusion that the reaction proceeds only on some part of the internal surface of the porous catalyst, in a zone of so-called 'internal diffusion'. The degree of use of a surface (h) can be defined as the ratio of the rate of the reaction in the 'internal diffusion' zone of the catalyst (i_{int}) to the rate on the whole surface of the porous layer (i_{total}):

$$\mathbf{h} = \mathbf{i}_{\text{int}} / \mathbf{i}_{\text{total}} \tag{2}$$

with the rate on the total surface of the porous layer calculated as below:

 $i_{\text{total}} = (\text{H/S}) (\text{k/ } D_{\text{effect}})^{1/2}$ (3)

where H – thickness of porous deposit, mm; S - geometrical surface of catalyst, mm²; k – coefficient of the rate of the reaction; D_{effect} – effective coefficient of diffusion of gaseous reactants in the porous layer [10]. A reaction order for hydrogen, according to [11], is close to 1. It is worth mentioning that the porous structure of grains of the catalyst is very complex and can be described only in statistical terms. To apply the equation (3), difficulty arises with the estimation of the value of D_{effect} , because the structure of the porous layer of the catalyst varies depending on the method of its preparation [12].

3. CATALYST CARRIER

Apart from the difference in the diffusion coefficients for hydrogen and oxygen, the kinetics of the catalytic reaction of hydrogen and oxygen recombination on a porous Pt catalyst is bound to be impacted by the following processes:

- counter flow of the product of the reaction (1) water vapor,
- Stefan flow, i.e. the movement of the species induced to flow by the decrease in the volume of gases, as the result of the reaction (1),
- the heat produced in the exothermic reaction (1).

The last process appears to be the most influential. The heat produced in the reaction causes gradients in temperature to arise both inside the catalytic layer and along the surface of the catalytic plate. Thus, the temperature in the reaction zone (inside the porous layer) should exceed the temperature on the catalyst surface and in the gaseous environment:

$$T_{por} > T_{surf} > T_{gas}$$
⁽⁴⁾

The exact values of the gradients between these temperatures depend on the material and structure of the catalyst carrier. Therefore, the material used as a carrier determines a whole range of important practical characteristics of the catalytic cartridge, such as the removal of heat, the volume and the weight of the catalytic block, the cost and even the safety of its use.

Catalysts used in PAR may be divided into two groups, according to their structures: a) single-phase catalysts in which the metal-catalyst is used as a carrier and b) double-phase and multi-phase catalysts in which the carrier and the catalytic layer are clearly separated by one or more geometrical boundaries.

To sum up the above, it is fair to say that the structure of the catalyst is a dominant factor in its effectiveness for recombination of hydrogen and oxygen. The design of PAR is rather simple: it is a vertically installed pipe with the catalytic block inside. The search for a catalyst with a more effective structure is a crucial element in modernizing PAR.

New types of catalysts, both single and double-phase, are presented below. These catalysts have been developed, tested and put into manufacturing by the company 'Russian Energy Technologies' in the last few years.

4. METHODS TO ESTIMATE THE QUALITY OF CATALYST

The research and tests on catalytic devices were carried out in a climatic chamber (CC), 86 1 in volume, which was equipped with systems for a) thermostatic control (with open bath circulators), b) preparation of gas mixtures, c) input and output of gases, d) analysis of hydrogen, e) measurement of local temperatures, f) temperature and gas homogenization in the whole CC volume. The detailed descriptions of the 'flow method' applied in this research and of the data processing are given in the second report of the authors to the Conference [13].

Individual samples of catalysts were tested in the CC atmosphere. Cartridges of 2 to 5 catalytic plates were placed into a small-scale recombiner device, a 'pipe' of square section 4 to 25 cm² in area and 35 cm in height. The rates of the reaction were established under conditions of a constant flow of gas through the CC in a stationary mode, when the concentration of hydrogen and local temperatures of the catalyst stabilized. The rate was calculated by the equation that reflected the gas balance in the system [13]. The conditions for the ignition of hydrogen were studied in the same CC.

From the experimental data the dependence of the recombination rate (I, ml/min) and local temperatures (T, 0 C) from the concentration of hydrogen under a stationary mode (Cstat, % v/v) was plotted. From these the specific rates, i.e. rates per 1 cm² of the gas flow entering the device (i, ml/min cm2), were calculated and compared for different catalysts. Data on local temperatures at different sites of the catalyst plate provided an insight into the thermal regime of working catalytic cartridges.

The data for i-C and T-C graphs were obtained at a pressure of 1 bar, a temperature of the gas in the CC of 25 0 C and at the humidity of the CC environment due to water produced by the recombination reaction (1).

5. 'PUTTING CATALYST' (PC)

'Putting catalyst' (PC) was produced by spreading a paste-like mixture on a mechanical carrier followed by heat treatment. The paste contained three components: 1) a suspension of Teflon powder in water stabilized by oxyethylated alkylphenol; 2) H_2PtCl_6 solution; 3) γ -AI₂O₃ powder. In some experiments a two-component mixture was used, when H_2PtCl_6 was first adsorbed on to porous γ -AI₂O₃.

During heat treatment (310°C) two processes took place: 1) thermal decomposition of the stabilizer into simple organic compounds (spirits, aldehydes, etc.), which reacted with H₂PtCl₆ producing highly dispersed platinum, and 2) sintering of the Teflon powder into a hydrophobic porous layer covering the catalyst. As a result, the catalytic layer on the carrier consisted of a binding component (Teflon) and a dispersed metal-catalyst (Pt) adsorbed on porous γ -AI₂O₃. This method of preparation of a hydrophobic catalyst (HC) was described in detail in [14]. Table 2 provides examples of two- and three-component mixtures for catalyst preparation.

A.Three-component mixture					
	Pt	γ-Al ₂ C	D ₃ Teflon		
Weight of component in	1.0	9.3	13.3		
a mixture applied to 1					
cm ² of carrier surface,					
mg					
Percentage of total	4.2	39.1	56.7		
weight of the mixture, %					
B. Two-component mixture					
	H_2 PtCl ₆ on γ -Al ₂ O ₃		Teflon		
Weight of component in	12.0	12.0			
a mixture applied to 1					
cm ² of carrier surface,					
mg					
Percentage of total	47.4		52.6		
weight of mixture, %					

Table 2. Ingredients of two- and three-component mixtures for catalyst preparation

As a carrier for the PC, we tested various metal grids, wires, sheets and foils, as well as 'sandwich' structures, for example, a metal grid on foil. In fact, the PC can be made with almost any carrier, provided it is adhesive and unaffected chemically or thermally. The PC can function in an environment of any humidity, including conditions of vapor condensation and even periodic immersion in water. In our tests, the performance of PC samples didn't deteriorate after many hours of exposure to water. At a hydrogen concentration 2 % v/v, the observed specific rates of recombination on the PC were in the order of 10 ml/min cm². It is important to point out that a PC is reliable only at a concentration of hydrogen no higher than 4-6 % v/v, because at temperatures above 400° C the binding of the catalytic layer to the carrier fails and it crumbles off.

There is another serious drawback to the use of a PC in recombiner devices. During its functioning in a wide range of temperatures we observed catalysts crumbling, splitting into layers and even completely disintegrating. This happens due to variation in the thermal expansion of different layers of double- and multi-phase catalysts. This caused premature 'ageing' of the catalyst and, in the worst cases, hydrogen ignition as exfoliating fragments of the catalyst heated up to a high temperature under an adiabatic regime. Such observations led us to conclude that single-phase catalyst structures were more promising for working conditions with high concentration of hydrogen in the environment.

6. HYDROPHOBIC CATALYST ON POROUS METAL CARRIER (HCm)

In selecting a new catalyst carrier we chose porous Ti sheets produced by powder metallurgy [15]. To the best of our knowledge, porous Ti hasn't been used before as a catalyst carrier. Compared with γ -Al2O3, a well-known carrier, porous Ti has a much smaller specific surface area, in the order of 0.1 m²/g compared to 100 m²/g for aluminum oxide. As was shown above, a specific surface area of 0.031m²/g for Pt(porous)/Pt deposit was quite sufficient for catalytic activity. Far from being a disadvantage, the small porosity of the catalyst carrier is preferable, because it reduces the sorption of water vapor, thus minimizing its negative influence on various characteristics of the catalyst. We used porous Ti sheets of thickness 0.9 mm and density 3.3 g/cm³, both as a carrier and as an adsorbent of dispersed Pt metal-catalyst. The density of the Ti sheets was 1.4 times less than the density of massive Ti and approximately 2.7 times less than the density of iron and steel. A hydrophobic catalyst on a porous Ti carrier was prepared with the same high-temperature technology as that used for PC, described above and in [14]. The detailed description of the catalyst HCm was given in [16].

Fig. 2 presents i-C curves for a pipe size $4 \times 4 \times 35$ cm with an HCm cartridge consisting of 4 catalytic plates and for the Siemens FR90/1-150 model of PAR (the data were calculated with the formula given in [6]). At hydrogen concentrations less than 4.5 % v/v the catalytic activity of the HCm is slightly below that of the Siemens model, but the comparison reverses in favor of the HCm at higher concentrations of hydrogen.

HCm, like all other lamellar catalysts, is liable to overheating. Normally, at hydrogen concentrations above 8 % v/v without special measures to cool the catalyst, ignition of hydrogen takes place. Curve 2 (fig.2) shows that the explosion occurred at C(H₂) 8.8 % v/v. At the moment of ignition a thermocouple at the lower part of the catalyst plate registered the temperature of 545° C, while the upper part of the plate was slightly cooler, at 480° C, and the temperature in the gas flow above the plates was registered at 143° C (fig. 3). The "explosion" point is marked with the radial ornament. It is remarkable that the highest temperature was registered at the lower part of catalyst plate, which indicates that the ignition of hydrogen took place at that location.

Concentration of hydrogen is not the only variable that affects thermal regime of working catalytic cartridge. More general characteristic that determines the critical concentration of hydrogen, at which overheated catalyst ignites hydrogen (C_{ign}), is the convection flow. The rate of convection flow depends on how much obstruction to the flow catalytic plates present. This is determined by density of

plates packing, by their height and roughness. All these factors are closely interconnected. Changing one of them, we inevitably influence another.



Figure 2. Specific recombination reaction rates vs. concentration of hydrogen for PAR model FR/1-90 (Siemens) (1) and for HCm cartridge (2).



Figure 3. T-C graph for the lower and upper parts of HCm plate and for gas flow above the cartridge.

7. HYDROPHOBIC CATALYST WITH METAL GRID SCREEN

Two questions arise: whether it is possible to achieve higher critical concentration of hydrogen C_{ign} for some catalysts, and whether the lamellar catalyst can function at $C(H_2)$ above 8-9 % v/v. The extensive research on this problem was carried out in the last 10 years in Germany by companies Framatom ANP [17], Siemens Aktiengesellschaft [18], Forschungzentrum Julich [19] and others. A number of proposals to mitigate the overheating of working catalyst and the risk of hydrogen ignition have been offered. Among these proposals were to reduce the amount of metal-catalyst on carrier's surface, or to cover the catalyst surface by various porous layers (metal oxides, zeolites, basalt crumbs), which were applied only to the lower part of the catalyst plate. The latter measure reduces diffusion of hydrogen and oxygen to the catalytic surface and in this way prevents the overheating in the area, where ignition of hydrogen takes place. Unfortunately, patents [17, 18, 19] do not provide any information about how these modifications affect other characteristics of catalyst, in particular, the reaction rate and PAR productivity.

In this research another way to prevent local overheating of catalyst was developed. To achieve more even distribution of recombination reaction along the catalyst plate, a screen cover of metal grid made of dense weaving (without mesh), the so-called 'filter grid', was applied to the surface of the catalyst. It has been established that such grid provides the best 'radiator' (heat-removing) effect and, at the same time, does not inhibit diffusion of hydrogen. To provide the full cover of catalyst plate by metal screen and to avoid direct contact between gas and catalyst plate, the edges of grid pockets were thoroughly welded. A detailed description of the preparation of hydrophobic catalyst with metal grid screen (HCm(screen)) is given in [20].

Data presented by figures 4 and 5 illustrate the kinetic activity and thermal regime of the catalyst HCm(screen). The i-C curves 2, 3 and 4 (fig.4) present data obtained at three different experiments using HCm(screen) catalytic plates (30x90 mm in size), prepared separately for every experiment. In comparison, the i-C curve 1 (dash line, up to $C(H_2) = 8 \% v/v$) presents data from [6] for Siemens PAR model FR/1-90.

The optimal structure of catalyst HCm(screen) has been found after a long search, by modifying various characteristics of the catalyst, such as length of plate, type of grid, density, structure of cartridge and others. As an example of undertaking experiments, the fig.4 presents two i-C curves, for experiments with plates 50 mm (5) and 130 mm (6) long. In both these cases the tests were interrupted by the explosion at hydrogen concentration between 17 and 18%v/v. These events are indicated by the radial ornament.

When the plates 90 mm long have been used, high concentrations of hydrogen were reached without ignition. The curves 2, 3 and 4 demonstrate that. Despite the dense weaving and the absence of any open mesh in the screen grid, in the range of hydrogen concentration 1 - 8 % v/v the HCm(screen) catalyst displays the activity that is very similar to FR/1-90 model of PAR (dash line 1, fig.4). Fig.4 demonstrates that HCm(screen) catalyst allows to reach hydrogen concentration above 20% v/v (curves 2,3 and 4), which is much higher compared to the model FR/1-90. This fact can be explained on the basis of the hypothesis, given above, about the prevalence of the diffusion of hydrogen compared to that of oxygen in the porous body of the catalyst. The porous grid in combination with the porous layer of catalyst creates conditions for further increase in hydrogen concentration in the Knudsen-type diffusion flow of gases through the catalyst, which facilitates the reaction of recombination.



Figure 4. i-C graph for recombination reaction at stationary conditions for FR/1-90 model [6] (dash line 1) and for experiments with 4-plate cartridges of HCm(screen) catalyst (2 - 6).



Figure 5. T-C graph for the lower and upper parts of HCm(screen) catalyst plate and for gas flow above the cartridge.

Fig. 5 offers an explanation to such behavior of HCm(screen) catalyst. T-C graph presents the data for one of the three tests from fig.4. The data for two other tests were almost identical to the displayed. It is remarkable, that in stark contrast to the fig.3, which shows thermal curves for HCm catalyst, the temperature of the upper part of HCm(screen) plate is much higher than the temperature of its lower part. At C(H₂) 20 % v/v this difference reaches almost 300° C. It is also noticeable that the local temperatures of both parts of the plate stabilizes above C(H₂) 15 % v/v, which most likely prevents the overheating of the catalyst.

Thus, the cover of the catalyst surface by a metal grid results in reversal of thermal distribution within the cartridge of catalytic plates. It also allows the catalyst to function at much higher concentrations of hydrogen. This, in itself, constitutes an essential progress for practical application of recombiner devices in various conditions. In addition, metal screen provides a better protection of catalyst against dust, condensate, fog, aerosols and other potential inhibitors of catalytic reaction.

CONCLUSIONS

Recombination reaction of hydrogen and oxygen with surplus of O_2 in the environment proceeds inside the porous phase of catalyst, where a surplus of H_2 is created due to high mobility of its molecules.

Catalyst with mono-phase metal structure is most effective in the range of high hydrogen concentration.

The porous Ti, produced by powder metallurgy, can be used as a strong, water-resistant and technologically cheap catalyst carrier.

A 'filter'- type grid, used as a screen of the catalytic plate, allows achieving a considerable improvement in the heat regime of the catalytic plate.

The innovative model of the catalyst HCm(screen) can function (without igniting hydrogen) under high concentration of hydrogen, up to and above 20% v/v, and with special rate of reaction reaching 400-450 ml/min cm² (21.6-24.3 kg/h m²).

The difference in mobility of O_2 and H_2 molecules under conditions of Knudsen diffusion is proposed as an explanation for the effectiveness of porous-Pt catalyst in recombination reaction.

Acknowledgements

Authors wish to acknowledge help of Dr. Vadim Kasatkin (Phisical Chemistry Institute of Russia Science Academy) in electrochemical experiments and of Mr. Alexander Sharapov and Mrs Tamara Potapova (the company 'Russian Energy Technologies') in preparation of catalysts.

REFERENCES

- 1. Smith A. Introduction to Inorganic Chemistry, 1, 3rd ed., New York (1917)
- 2. Scherbakova M.V., Shepelin V.A., Dzisjak A.P., Alfimov V.I., Chemical Industry (USSR), 1986 год, N3, page 167; 1988, N7, page 406;
- 3. Heck R., Hill A., A two-pronged approach to hydrogen reduction, *Nuclear Engineering*, 37,1992, p.21-26.

- 4. Ferroni F., Chakraborty A.K., 1996. Design comparison of devices for catalytic removal of hydrogen. In: *Proceeding of the International Conference on Nuclear Containments*. Cambridge, UK.
- 5. Shepelin V.A., Zalkind Tc.I., Veselovski V.I., *Soviet Electrochemistry*, Interaction of H₂ and O₂ on Pt. 1.Reaction kinetic, *Soviet Electrochemistry*, 4, 1968, N8, pp. 975-978.
- 6. H₂ recombination system. Framatome ANP technical offer of Belene nuclear power plant. Part II. Technical description. ASE. 2005.
- 7. Shepelin V.A., Zalkind Tc.I., Veselovski V.I., Interaction of H₂ and O₂ on Pt. 1.Reaction mechanism, *Soviet Electrochemistry*, 5, N11, 1969, pp. 1291-1296.
- 8. Vinnikov Ju. Ja., Shepelin V.A., Veselovski V.I. Photoelectrochemical and ellipsomertic study of surface oxides on Pt, *Soviet Electrochemistry*, 9, N10, 1973, pp. 1557-1562.
- 9. Delahay Paul, Double layer and electrode kinetics, 1965, John Wiley&Sons Inc., N-Y, Sidney, London.
- 10. Egerev V.K. Diffusion kinetic in motionless environmenrts, 1970, Publishing House «Nauka», Moscow..
- 11. Boreskov G.K., Slin'ko M.G., Chesalova V.S., *Phisical chemistry Journal* (USSR), 1956, 30, N12, page 2787-2793.
- 12. Frank-Kamenetskiy D.A.. Diffusion and heat transport in chemical kinetic, 1967, Publishing house «Nauka», Moscow (USSR).
- 13. Shepelin V., Koshmanov D., Efimova N., Safe testing of the catalytic devices in hydrogen-air flow, *Proceedings of the Third ICHS 2009*.
- 14. Shepelin V.A., Etkina L.I., Kasatkin E.V., Kotina G.V., Kuraev A.L., *Chemical Industry (USSR)*, 1995, N3, pages 11-15; Patent SU 1747146 A1.
- 15. Antsiferov V.N., Powder industry and power covers, 1987, Moscow.
- 16. Koshmanov D.E., Shepelin V.A., Patent application (Russia) N2008101609/04(001767), 2008
- 17. Eckard B.,Berndt M.,PCT/DE2000/000797 (15.03.2000).
- 18. Eckard B., Hill A., PCT/DE2000/000798 (15.03.2000).
- 19. Brockerhoff Peter, Werner Von Lensa, Reinicke Ernst Arndt, Patent US 6,846,775 B1, 2005.
- 20. Koshmanov D.E., Shepelin V.A., Sharapov A.G., Patent RU 77 488 U1, 2008