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# Humidity induced deactivation of $Al_2O_3$ and $SiO_2$ supported Pd, Pt, Pd-Pt catalysts in $H_2 + O_2$ recombination reaction: The catalytic, microcalorimetric and DFT studies

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ABSTRACT

The thermal effects and activity of silica and alumina supported monometallic Pd, Pt and bimetallic Pd-Pt catalysts (of various Pd/Pt ratio) in the exothermic $H_2$ and $O_2$ recombination reaction have been investigated in view of their potential use in the industrial passive autocatalytic recombiners (PAR). The pattern of changes in both the heat evolution and the conversion of hydrogen observed in the $H_2/O_2$ reaction seem to reflect the effect of water formation on the activity/deactivation of the studied catalysts. The catalysts have been prepared using the colloid-based reverse “water-in-oil” microemulsion method and characterized by XRD, XPS, SEM, EDS techniques. The recombination reaction of hydrogen and oxygen has been monitored using Microscal gas-flow through microcalorimeter as well as a laboratory flow microreactor. The humidity present in the reaction mixture and the water molecules formed in the recombination reaction both inhibited the activity of the tested catalysts. The nature of support and the type of metal played a role in such water-poisoning effect. Deactivation of alumina supported catalysts was stronger than silica supported counterparts and Pt was more prone to the water inhibition compared to Pd. The most promising catalysts exhibiting the lowest amount of evolved heat accompanied by high and stable activity are silica supported Pd-rich bimetallic Pd-Pt particles whereas alumina wash-coat-Pt is the catalyst of chose in the PAR reactors. The observed activity/water-poisoning relations found confirmation in the DFT calculations concerning the interactions between water molecules and mono-(Pd, Pt) as well as bi (Pd-Pt) metallic clusters as a function of cluster size and Pd/Pt compositions.

## 1. Introduction

Passive autocatalytic recombiners (PAR) are the safety devices applied at an industrial stage of development in the nuclear plant containments to lower the explosion risk associated with hydrogen release. The idea of using PAR is to recombine catalytically hydrogen and oxygen according to strongly exothermic $H_2 + 0.5\ O_2 = H_2O + 240$ kJ/mol reaction. In water-cooled nuclear reactors, under normal and emergency operating conditions the radiolysis process in water as well as vapor-metal reactions are the source of hydrogen which is released into air-filled containment atmosphere. These hydrogen generating processes are accelerated as metal elements of construction being in contact with coolant are exposed simultaneously to high temperature and radiation.

However, a massive hydrogen generation may take place during severe accidents in nuclear plants. This can be caused by overheating of the reactor core above 1000 °C, and consequent oxidation of the zircaloy (an alloy of zirconium and tin) with water, generating massive hydrogen release into the air-filled containment atmosphere. Core meltdown accidents in nuclear power plants, TMI-2 in 1979 and more recently the Fukushima accidents (2011) showed the importance of addressing the hydrogen risk in the design and safety case of nuclear reactors [1]. Several solutions have been considered to avert the hydrogen explosion risk and in the current work, the option based on PAR reactors is considered to be the most promising.

The PAR reactors are “passive”, i.e., they are self-starting and self-feeding, they act with no need of any external power supply and no human intervention. The gas mixture flows through the recombiner by natural convection. The heat evolved in the hydrogen recombination reaction produces the temperature difference which induces a natural convection flow through the reactor. The

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existing PAR designs mostly use a series of plate type reactors consisting of thin metal (e.g. stainless steel) plates coated with an alumina wash coat and platinum or palladium. A role of this plate-type structure is to optimize the circulation of gasses in contact with the catalyst. The other types of catalytic recombiners consisted of spherical granules of a ceramic carrier (e.g. alumina) coated with Pd, porous catalyst material (cordierite $2MgO\ 2Al_2O_3\ 5SiO_2$) in the shape of honeycomb coated with platinum [1,2].

However, certain problems are encountered on using the commercially available PAR reactors. At massive hydrogen release (concentration of hydrogen above 7–10%) as in case of severe accident, the recombiner can overheat due to the large exothermic effect of the recombination reaction and thus PAR reactors may become an ignition source itself. This problem has been studied mainly by the numerical simulation of hydrodynamic conditions and hydrogen mitigation in catalytic recombiner [1–6]. Several analytical models have been developed to study the recombiner behavior with regard to detailed fluid kinetics, hydrogen and temperature distribution along with the recombination process. For the analysis of the processes inside a PAR such as reaction kinetics or heat and mass transfer a 3D in-house code has been developed [6]. This model has been verified by experimental data obtained using box-type recombiner built of parallel plates with alumina wash-coat Pt of various metal particle size. From the operation of catalyst checked by measuring the hydrogen recombination rate together with the temperature of catalyst surface, the authors concluded that the Pt coating density on non-porous support resulting in high density of evenly distributed metal particles is better for efficiency [5]. In this context the catalysts with well dispersed Pt particles deposited on the nickel foam coated with an alumina wash-coat were tested in the flow reactor using the bed of catalyst [13]. Performance of these catalysts was determined by the contents of alumina/platinum and optimization of catalyst composition (45 wt% $Al_2O_3$ wash-coat and 3 wt% Pt) allowed complete removal of hydrogen at hydrogen concentration of 4 vol.%. Moreover, by using this foam-based catalyst the hydrogen risk was avoided.

Furthermore, the PAR reactors should come into action spontaneously as soon as the hydrogen concentration begins to increase in the containment atmosphere. However, conventional recombiners show a considerable time delay [7] which may also lead to accumulation of explosive gas products leading to an unintended ignition of hydrogen/air mixture. This delay is partly associated with the distance from the hydrogen source. However, it is mostly induced by the water film covering the catalyst which is formed because of relatively high level of water vapor in the PAR atmosphere. Water films can result from spray droplet deposition or steam condensation on cold walls. On catalytic surfaces that are covered with a “water film” the catalytic recombination cannot start. Once a partly wetted surface is exposed to hydrogen, the dry portions are heated up by the catalytic recombination and the water film at adjacent surface parts is evaporated due to heat conduction inside the catalyst. The dry spots grow until the entire surface is dry and under catalytic reaction. Once the catalytic reaction has started and the coated surface temperatures are at a level of several 100 °C, wetting by spray droplets will not be possible. Therefore, water is considered to be a poison for catalysts and the problem of water in the performance of PAR reactors has been also taken into account in the publications reporting numerical modeling [6].

It should be pointed out that water is also formed as the product of recombination reaction. Expectedly, its interaction with catalyst may be of crucial importance, in particular when the hydrogen concentration is low and the heating of catalyst surface due to the heat evolved in the recombination reaction is not high enough.

Although the available literature data reporting catalytic performance in terms of activity/deactivation in the PAR reactors are rather scarce [8–14], they concentrate on the Pt, Pd and Pt-Pd catalysts. The catalysts comprising the particles of Pd, Pt or Pd-Pt dispersed finely on strips of corrosion resistant stainless steel wire gauze [10,11], cordierite honeycomb [9], and large area polymeric sheet [8] were evaluated for $H_2/O_2$ recombination in laboratory and in the pilot plant reactor. Their resistance to poisons such as CO, $CO_2$, $CH_4$ and water vapor strongly varied, being influenced by a lot of parameters, including the geometry of catalyst bed, the type of support and the type of metal [8,10–12]. The authors of ref. [12] used the Pd, Pt, and Pd-Pt particles deposited by electroless reduction with formaldehyde on stainless steel wire gauze for tests carried out under static air conditions. The catalysts exhibited similar activity but they differed in deactivation due to the poisons such as CO, $CO_2$, $CH_4$. Water caused a temporary deactivation of Pt or Pd-particles. Carbon monoxide induced also deactivation, more pronounced for palladium catalyst. The Pd-Pt mixed catalyst was found to exhibit the best stability. Its activity remained almost unaffected by the presence of such poisons [12]. On the other hand, the effect of water poisoning was almost completely excluded on a polymeric sheet-based Pt catalyst [8,15] because of a hydrophobic nature of the polymeric carrier. Catalytic performance was also related to the surface morphology of metal particles. Better performance was observed for rough and round agglomerates of mixed Pd-Pt particles compared to smooth, spherical Pt particles [12]. Among alumina supported Pd, Pt and bimetallic Pd-Pt model catalysts, the Pd-Pt/$Al_2O_3$ catalyst exhibited the best resistance to other type of poison, namely iodine compounds (diiodine, methyl iodine) appearing among various fission products [14]. The Pt/$Al_2O_3$ catalyst was most strongly poisoned by such compounds.

In the present paper we focus on the problem of metal and support selection for the hydrogen and oxygen recombination reaction taking into account interactions of catalysts with water molecules. Water released during recombination reaction as well as water present in the reaction mixture ($H_2$ in air) entering the catalyst bed, are both considered. Alumina and silica supported monometallic Pd, Pt catalysts as well as the bimetallic Pd-Pt catalysts of various Pd/Pt ratios have been studied. We focus our attention on certain practical aspects of real life catalysts performance.

The activity/deactivation effects reported in the literature were evaluated for the $H_2/O_2$ recombination reactions studied using typical fixed-bed flow reactor [13,14], static air conditions [8–12], reactor comprising of plates [5]. In general, in all these catalytic tests, a $H_2$–air mixture was introduced into contact with the catalyst at room temperature and the progress of recombination reaction was monitored by measuring hydrogen conversion and the temperature rise on the catalyst bed. In the present work, the performance of catalysts is studied in the conventional fixed-bed flow reactor and the conversion of hydrogen together with the rise in temperature of catalyst bed is monitored. Moreover, thermal effect generated during recombination of hydrogen and oxygen is evaluated by gas flow-through microcalorimetric method. The microcalorimetric method has already been used for evaluation of Pt catalysed combustion of hydrogen in air [16]. The kinetic data provided by this technique agrees well with those obtained by conventional methods. Here, reaction mixture of various $H_2$ concentrations (6.2–9.4%) in air is introduced at temperature of 22 °C into the calorimetric cell containing the catalyst sample. The conversion of hydrogen and the heat evolved are monitored.

In order to recognize a role of water in activity/deactivation of studied catalysts the interactions of water molecules with mono-(Pd, Pt) and bi (Pd-Pt) metallic clusters consisting of various number of metal atoms $M_n$ ($n = 2$–26) are calculated within the DFT method, implemented in Turbomole code. The calculations concentrated on a role of their size and chemical composition in the interaction with water molecules.