

Catalytic activity of Pd-Ni in the oxidation of hydrogen for the safety of nuclear power plant

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Pd-Ni/Al₂O₃ systems were investigated in the reaction of hydrogen oxidation in terms of their possible application as catalysts used in passive autocatalytic recombiners (PARs) used in nuclear power plants. Testing experiments were carried out in a flowing system at different temperatures and humidity of the reaction mixture. The bimetallic catalysts exhibited higher response to the increase of temperature and higher resistance to inhibit water than the monometallic palladium catalyst. They showed excellent stability during a few tens of hours, similarly, like their monometallic counterpart. Our bimetallic catalysts of hydrogen oxidation can be used as cheaper alternatives to catalysts based on the precious metals in the hydrogen oxidation without loss of their activity over time.

Keywords: palladium, palladium-nickel, catalyst, hydrogen oxidation.

INTRODUCTION

The vital component of zircaloy, the construction material of the nuclear reactor equipment, is zirconium. This element is characterized by very low absorption of thermal neutrons and has high corrosion resistance, however at higher temperatures it reacts with water forming hydrogen. Hydrogen causes hydrogen embrittlement of fuel cladding for long lasting exposure and the risk of explosion during the reactor overheating. Hydrogen oxidation reaction plays a crucial role in safe removing of dangerous hydrogen from the nuclear reactor area, where passive autocatalytic recombiners (PARs) are used.

It is well known that platinum and palladium are the best catalytic metals for hydrogen oxidation. Other transition metals are also active but their performance is inferior to that of Pt and Pd^{1, 2, 3, 4}. Application of precious metals in passive autocatalytic recombiners must add to their overall cost. The natural thing is to search for cheaper effective alternatives to platinum and palladium. Because it cannot be reached by application of monometallic systems we decided to investigate bimetallic catalysts. We assumed that successful replacement of a considerable part of these noble metals (Pt, Pd) by some cheaper elements would definitely contribute to reduction of catalyst's cost. Testing such a possibility has prompted us to study the catalytic activity of Pd-Ni system in the oxidation of hydrogen. Although Pd-Ni alloys are practically completely miscible *fcc* solids, it seems to be a general agreement that the surface layer of Pd-Ni particles is highly enriched in palladium^{5, 6}. However, the underneath layer is composed of nearly pure nickel⁵. Both facts appear to be crucial in the genesis of our research. First, location of a more active alloy component in the surface layer should have a positive impact on its catalytic reactivity. Second, if the second layer is composed of mainly nickel, which differs from palladium by the atomic size, leading to a sandwich structure, then such surface layer should experience a considerable stress⁷. It was shown that this stress would positively modify catalytic properties of palladium⁸. Density functional theory calculations performed to study of CO oxidation on palladium and Pd-Ni alloys with sandwich structure demonstrated that partial replacement of palladium by

cheaper nickel in the catalyst should lower activation energy of oxidation and reduce the cost of the catalyst⁹. Introduction of nickel to palladium catalysts makes a substantial impact on catalytic properties also in other types of chemical reactions, e.g. in catalytic reduction^{5, 10, 11} or in hydrodechlorination^{12, 13}.

In our work the catalytic behavior of Pd-Ni in oxidation reactions was crucial, so the results of Kantalar Neyestanaki and Lindfors, where Pd-Ni/silica-fibre catalysts showed higher activity than Pd/silica-fibre catalyst in methane combustion¹¹, were found particularly interesting. The interpretation of these results was based on the specific sandwiched assembly of Pd/Ni surface where the stress generated by different atomic sizes of both metals modified the electronic structure^{11, 14}.

Our preliminary results showed that alumina-supported Pd-Ni catalysts would be regarded as respective replacements for expensive platinum or palladium catalysts for hydrogen oxidation¹⁵. This paper is an extension of the previous work. Here we focused on practical aspects of possible future application of Pd-Ni catalysts. To this aim we describe the results of long-term testing of Pd-Ni/Al₂O₃ catalysts at higher conversions and their behavior in the reaction mixture characterized by a different degree of humidity. Both tests appear to be important prior to putting into practice new catalysts devoted for passive autocatalytic recombiners.

EXPERIMENTAL

Catalyst preparation

Preparation of Pd/Al₂O₃ and Pd-Ni/Al₂O₃ catalysts was described elsewhere¹⁵. Briefly, the desired base catalyst (2% Pd/Al₂O₃) was prepared by dry impregnation of γ -alumina (Sasol Puralox Scca-150/200), precalcined at 350°C for 2 h, with BET surface area \sim 200 m²/g with acetylacetonate precursor Pd(acac)₂ (Sigma-Aldrich, 99%) dissolved in toluene. After impregnation, the wet material was dried at 120°C, calcined in a flow of air at 400°C, and reduced in H₂ at 400°C for 4 h. Following reduction, the catalyst was passivated in H₂O-saturated helium flow at room temperature for 24 h and purged in He for next 24 h, and kept in a desiccator. The bimetallic

catalysts (2% Pd-Ni/Al₂O₃) were prepared by deposition of nickel particles on received monometallic catalyst as described earlier¹⁵. To achieve intimate contact of both metals uncovered (i.e. not carrying Pd particles) alumina centres were blocked according to the procedure earlier described^{16, 17}. After adsorption of H₂ at 70°C, the base Pd/Al₂O₃ catalyst was immersed in toluene and acetylacetonone (puriss, Fluka), where acetylacetonone was expected to block the surface of Pd-uncovered alumina, allowing subsequent deposition of nickel acetylacetonate (Sigma-Aldrich, 95%) on previously anchored palladium species. After the deposition, calcination in air at 400°C for 2 h, short purging in He, and reduction in H₂ at 400°C for 2 h were performed. Finally, the passivation with He/H₂O mixture was performed, followed by purging in He and drying as for the base catalyst mentioned above. A series of Pd-Ni/Al₂O₃ catalysts with Pd atomic contents of 70, 80, 90 and 100% were synthesized in the same manner.

Catalyst characterization

Characterization of Pd/Al₂O₃ and Pd-Ni/Al₂O₃ catalysts was performed using XRD and TPR and described earlier¹⁵. The main conclusion from those studies was that the prepared and reduced Pd-Ni/Al₂O₃ catalysts were highly dispersed (metal particles of 2–4 nm in size) and both metals are well mixed¹⁵. Table 1 recalls their basic characteristics.

Table 1. Composition of the catalysts

Catalyst	Symbol	Pd [wt%]	Ni [wt%]	Particle size [nm]
Pd/Al ₂ O ₃	Pd100	2.00	0	1.9
Pd90Ni10/Al ₂ O ₃	Pd90	2.00	0.122	2.6
Pd80Ni20/Al ₂ O ₃	Pd80	1.99	0.275	2.9
Pd70Ni30/Al ₂ O ₃	Pd70	1.99	0.470	3.7

Catalytic activity

The catalytic recombination of hydrogen with oxygen from air was performed in a flowing system under atmospheric pressure, with the concentration of hydrogen beyond the explosion region¹⁸. The flow of reactant consisted of a mixture of 0.50% H₂/synthetic air (analysis class 1, from Linde) was regulated by a mass flow controller (Bronkhorst). The flow of the reaction mixture was 25 ml · min⁻¹, apart from the experiments with dry reaction mixture when the flow was 100 ml · min⁻¹. For experiments with wet reaction mixture, the reactant flow was permitted to pass through a saturator with water (bubbler), before entering the reactor.

Kinetic experiments at different partial pressures of water consisted of flowing the reaction mixture (0.50% H₂/air) through the saturator with water maintained at a suitable temperature.

The catalyst (~100 mg) was deposited in a U-tube fitted with a fritted disc and thermocouple well. The course of hydrogen consumption was followed by a computer-controlled quadrupole mass spectrometer with electron multiplier (Ametek-Dymaxion). The reaction temperature was controlled with a temperature controller (Digi-Sense, Cole-Parmer) and recorded by the data collecting system of the mass spectrometer. Prior to the reaction, the samples were additionally reduced in H₂ at 400°C

for 0.5 h, purged in He at the same temperature and cooled to room temperature. Then, the reaction runs were started and investigated over longer periods. For the experiments at wet conditions the reaction mixture (flow: 25 mL · min⁻¹, space velocity: 0.03 s⁻¹) was passing through a bubbler with water maintained at a selected temperature to ensure a proper partial pressure of water (0.90, 1.4, 1.9, 2.3 kPa). The progress of reaction was monitored by collecting the mass signal of hydrogen (m/z = 2). Consumption of hydrogen was calculated after subtraction of background signal from the vacuum chamber and taking as baseline signal out of the reactor. To check the catalyst stability at dry conditions at 25°C, hydrogen consumption was checked at fixed intervals (1, 20, 25, 45, 50 and 70 hours from the start of the experiment). Next, experiments at higher temperatures were performed to check activity of Pd-Ni catalysts at higher temperatures. Because of high activity of the examined catalyst, the higher flow of the reaction was used (100 mL · min⁻¹, space velocity: 0.1 s⁻¹) to ensure lower than 100% conversion. After setting the required temperature (25, 50, 60 and 70°C), the signals of hydrogen and temperature were collected. To present the inhibiting effect of water additional experiment was performed on the catalyst Pd90. First, the reaction mixture was passed over the dry catalyst, then additionally through the bubbler with water (2.3 kPa, wet conditions) and again only through the catalyst with bypassing the bubbler (recovery of dry conditions).

RESULTS AND DISCUSSION

In this paper we wish to compare the activity of Pd-Ni/Al₂O₃ catalysts with the monometallic Pd/Al₂O₃ catalyst in the reaction of hydrogen oxidation at different wet conditions, check the long-term stability at dry conditions and activity at different reaction temperatures.

Basic characterization of the catalysts used here was presented in our previous report¹⁵. The synthesized Pd-Ni/Al₂O₃ catalysts reached high dispersion with metallic particles of 2–4 nm (recalled in Table 1) as measured by H₂ chemisorption. Good intermixing of the active components was indicated by the temperature-programmed reduction (TPR) and X-ray diffraction studies¹⁵. In the TPR profiles, single bell-shaped profiles were observed at low reduction temperatures (0–100°C) with an absence of negative peaks from a β-PdH phase decomposition suggesting good mixing of both metals and an apparent absence of unalloyed nickel species¹⁵. This indicates that the applied catalyst preparation method led to deposition of both metals (Pd + Ni) in a close vicinity, allowing their alloying at the reduction conditions. On the other hand, catalyst calcination at 400°C does not cause any serious separation of both metals. In an opposite case, separated Ni (or NiO) species would be transformed to Ni aluminate, which was not observed in the TPR spectrum¹⁵.

Water as a product of the reaction as well as introduced with the reaction mixture inhibits the rate of recombination reaction² which was confirmed by our experiments. The influence of humidity of the reaction mixture on reaction was explored by changing the partial pressure of water in the gas stream. It was found (Fig. 1)

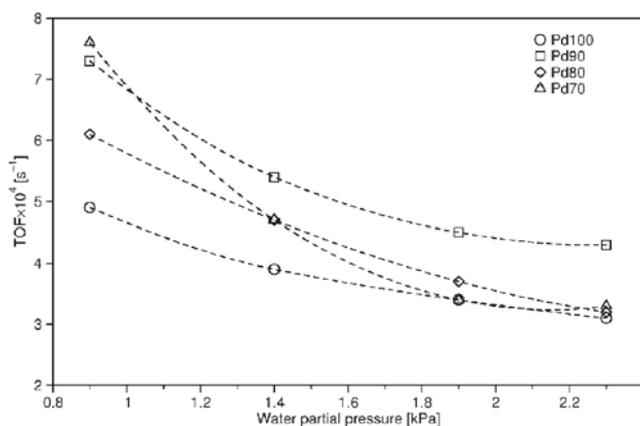


Figure 1. The effect of water partial pressure on the activity (TOF) of the catalysts in the reaction proceeded at 25°C; flow of reaction mixture: $> 25 \text{ mL} \cdot \text{min}^{-1}$

bimetallic catalysts, especially the catalyst with the lowest concentration of nickel (Pd90), exhibit higher resistance to water than palladium-only catalyst. Addition of nickel to palladium catalyst probably hinder the adsorption of water competing with hydrogen.

The inhibiting effect of water and recovery of the activity of bimetallic catalyst (Pd90) catalyst was presented on Figure 2, where the signal of hydrogen during switching the dry and wet reaction mixture through the catalyst is demonstrated. Valve turns to allow inflowing of the reactants to the reactor are marked with black triangles, whereas empty triangles indicate bypassing of the reactor. It is clear that the sharp negative minima (“spikes”) in the signal $m/z = 2$ are caused only by the first type of turns, not from bypassing of the reactor. The vertical bars show the consumption of hydrogen which is high at dry, low at wet conditions and becoming gradually higher after switching from wet to dry reaction mixture. Therefore, it appears that excess of water reduces the catalytic activity of Pd-Ni catalysts, however it is easily released from catalyst’s surface at dry conditions, making the catalyst much more active. At dry conditions the consumption of hydrogen decrease asymptotically to almost constant value over 1 h reaction and with water (partial pressure: 2.3 kPa) in the reaction mixture this

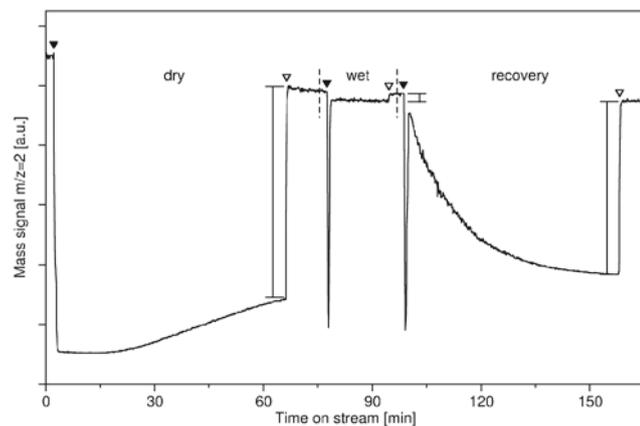


Figure 2. Mass signal of H_2 ($m/z = 2$) during reaction in dry conditions, wet conditions and during drying (recovery of conversion) at 25°C; flow of reaction mixture: $25 \text{ mL} \cdot \text{min}^{-1}$. Valves turns allowing the entrance of the reaction mixture the reactor are marked by filled triangles and valves turns to bypass by empty triangles. For explanation, see text

consumption drastically drops to the low level. Then, at the dry reaction mixture a recovery of the conversion proceeds and catalyst after 1 h drying in the reaction mixture at room temperature returns to the almost initial hydrogen conversion.

Figure 3 shows the relation between the activity expressed in TOF and reaction temperature at dry conditions. We decided to investigate the performance of all tested catalysts at the conditions of high conversion. Such an approach does not allow to assess such kinetic parameters like reaction orders or activation energies, however it should allow to assess the practical value of Pd-Ni catalysts. The activities of the tested catalysts at room temperature are similar, but at higher, more realistic reaction temperatures, the activity of the tested catalysts rises more steeply for bimetallic systems, especially for the most doped with nickel Pd-Ni catalyst (Fig. 3).

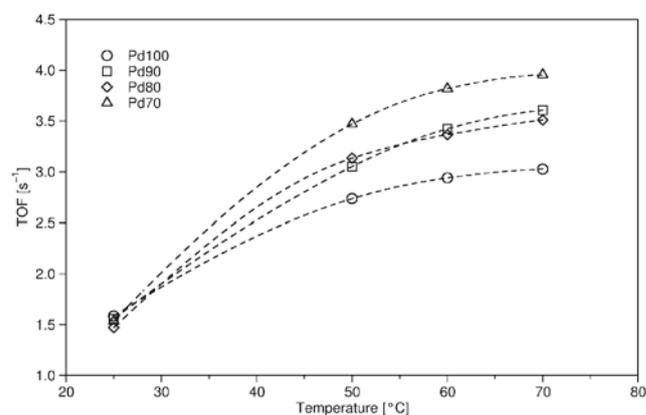


Figure 3. Activity (TOF) at dry conditions vs reaction temperature. Flow of reaction mixture $100 \text{ mL} \cdot \text{min}^{-1}$

The stability of our Pd-Ni/ Al_2O_3 catalysts in comparison to Pd/ Al_2O_3 was checked at room temperature for 70 hours (Fig. 4) with probing the depletion of hydrogen in the reaction mixture stream at intermediate intervals. The bimetallic catalysts offer an excellent stability over time just as Pd-only catalyst but slightly lower conversion. Long lasting recombination reaction does not change catalytic worth of our bimetallic, cheaper, catalysts. Their conversions at room temperature reach $\sim 65\%$ and this value is constant over time.

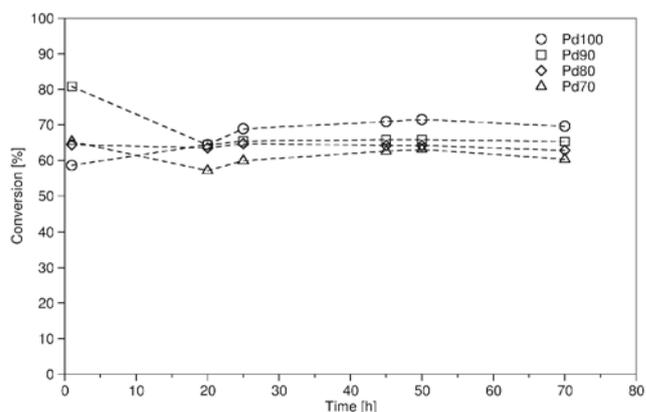


Figure 4. Stability of the catalysts with time on stream at 25°C; flow of reaction mixture $25 \text{ mL} \cdot \text{min}^{-1}$

CONCLUSIONS

Pd-Ni/Al₂O₃ catalysts, prepared to achieve good metal alloying, showed high activity and stability over time in the recombination reaction of hydrogen and oxygen. Their excellent stability allows replacing of expensive precious-only catalysts in passive autocatalytic recombiners.

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