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Electrochemical promotion of Bi-metallic Ni₉Pd core double-shell nanoparticles for complete methane oxidation



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ABSTRACT

Electrochemical promotion of Ni₉Pd nanoparticles (NPs) with low Pd content (Ni:Pd = 9:1 atomic ratio) supported on yttria-stabilized zirconia (YSZ) solid-electrolyte was evaluated for the first time for complete methane oxidation. Electron Energy Loss Spectroscopy (EELS) showed a Pd core with a Ni first shell surrounded by 3–4 nm layer of Pd outer shell. This core double-shell structure of Ni₉Pd NPs enhanced the catalytic activity and stability compared to mono-metallic Pd and Ni NPs under open-circuit. The reversible electrochemical promotion of Ni₉Pd was obtained upon positive polarization between 425 and 500 °C. At 425 °C, the reaction rate increase reached 240% corresponding to apparent Faradaic efficiency of 25. On Ni₉Pd NPs the reaction exhibited electrophobic behavior, i.e., the rate increased with anodic polarization, under all experimental conditions of this study. The results demonstrate the advantage of using Ni₉Pd bi-metallic nanoparticles with core double-shell structure for methane complete oxidation due to the synergetic effect between Pd and Ni and very low amount of expensive Pd phase. EPOC with this type of highly dispersed and low noble metal content catalysts may find a way in the real world catalytic converters for gas exhaust treatment.

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1. Introduction

Natural gas (NG) has attracted considerable attention as an alternative fuel due to its high energy density and low environmental impact [1]. NG is already used in natural gas engines in particular natural gas vehicles (NGV) [2]. Depending on its source, NG consists of 90% of methane, which in comparison to gasoline has a low carbon emission per energy produced [3]. Methane is a very stable molecule and the activation of C-H bond represents a challenge, often resulting in release of unburned methane into the atmosphere. Because CH₄ has 23-fold greenhouse effect compared to CO₂, this makes its full combustion critical to prevent any unburned methane release into the atmosphere [4]. Therefore, to continue to be attractive, NG engines must be associated with post-treatment systems in order to reduce their pollutant emissions by unburned methane. Thus, development of a solution for total elimination of unburned methane residuals has attracted a great attention and would give a real advantage to the NGV industry.

Catalytic combustion of methane at low temperature (<550 °C) have been the interest of a number of studies as no thermal NO_x would be produced [5]. The competition between complete and partial oxidation of methane takes place above 550 °C (at a ratio exceeding 2-to-1 CH₄/O₂) [6], whereas low to no selectivity towards partial oxidation is found below this threshold [7]. Several catalysts have been investigated for the complete methane oxidation such as palladium [8–11], platinum [12,13], rhodium [14] and perovskites [15]. Amongst these catalytic systems, palladium was found to be the most active catalyst at temperatures below 550 °C [9].

The activity and stability of Pd catalysts can be increased by adding a second metal to form a bi-metallic PdM catalyst [16]. In particular, the addition of Ni to Pd either in the form of bimetallic catalyst or the support lead to the enhanced catalytic activity and stability of Pd [17]. Persson et al. studied the influence of adding various metals (Co, Rh, Ir, Ni, Pt) to Pd (synthesized by incipient wetness technique) for the methane oxidation [18]. The authors showed that addition of Ni resulted in superior activity compared to other metals due to the improved thermal stability of PdNi, even though the activity was inferior to that of Pd alone [17,18]. Similar results were found when Pd was supported on nickel-alumina

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support, which resulted in particle size decrease [19]. In addition, Shen et al. studied the effect of different nickel-palladium synthesis methods and showed improvement of the catalytic rate when polyol synthesis was used instead of the conventional impregnation technique [20]. The polyol method resulted in highly active Ni/Pd bi-metallic NPs supported on alumina compared to less active Pd on NiAl₂O₄ spinel phase.

Furthermore, the activity and stability of Pd can be improved using electrochemical promotion of catalysis (EPOC) phenomenon. EPOC or Non-Faradaic electrochemical modification of catalytic activity (NEMCA) effect is a general phenomenon in catalysis, where the rate of the catalytic reaction and in some cases reaction selectivity are modified (promoted or inhibited) by current or potential application. In this case, the catalyst also serves as a working electrode in the solid-state electrochemical cell that uses ionic $(O^{2-}, Na^+, H^+, OH^-, etc.)$ conductor as a solid-electrolyte. As shown using various spectroscopic surface sensitive techniques. this effect is due to electrochemical pumping (removing) of ionic species to (from) the gas-exposed catalyst surface [21-24]. Addition of ionic promoters results in the variation of the catalyst work function (WF) due to an electrochemically controlled migration of ionic species towards (from) the support [25,26]. The change in WF leads to modification of the adsorption strength of reactants and/or intermediates that in turn has a significant effect on the catalytic rate under closed-circuit conditions. The ratio of the closedcircuit rate, r, over the open-circuit rate, r_0 , is known as the rate enhancement ratio, ρ :

$$\rho = \frac{r}{r_o} \tag{1}$$

Another parameter used to quantify EPOC effect is the apparent Faradaic efficiency, Λ which shows if the observed rate increase (decrease) is faradaic, i.e., due to electrochemical reactions, $\Lambda \leq 1$ or non-faradaic due to electrochemically induced migration of promoters, $\Lambda > 1$:

$$\Lambda = \frac{r - r_o}{l/nF} \tag{2}$$

where r is the reaction rate under polarization (mol O/s), r_o is the reaction rate under open-circuit condition (mol O/s), I is the current (A), n is number of electrons and F is the Faraday's constant.

EPOC of methane complete oxidation have been investigated using several catalysts, such as Pt [27], Rh [28,29], Pd [30,31] and Au and Ag [32]. Similar to conventional catalysis, Pd showed the highest catalytic activity at lower temperatures [30–35]. Roche et al. reported NEMCA studies of methane combustion on Pd deposited by physical vapor deposition (PVD) on YSZ. They demonstrated Faradaic efficiency of 2.4 under positive potential $(U_{WR} = 1 \text{ V})$ application and a reaction mixture of CH₄/O₂: 2/10% at 500 °C. The increase in the Faradaic efficiency occurred with the increase of the catalyst thickness, however it resulted in decrease of mass activity. In Matei et al., NEMCA effect was studied for thin Pd film catalysts deposited by impregnation technique on dense and porous YSZ solid-electrolyte disk [33]. The rate enhancement ratio, ρ , of 1.2 and apparent Faradaic efficiency, Λ , of 17 was obtained under galvanostatic polarization (I = 5 mA) at 400 °C. Jiménez-Borja et al. investigated NEMCA effect for methane combustion on Pd/YSZ film catalyst with and without CeO₂ interlayer [36]. Addition of ceria interlayer led to significant reaction rate increase compared to Pd/YSZ due to oxygen storage capacity of ceria and stabilization of PdO active phase. The authors showed stable electrochemical promotion with the rate enhancement ratio up to 2.1 at 470 °C, when CH_4/O_2 : 0.4/1% ratio was used [37]. In all previous EPOC studies of methane complete oxidation on Pd, an electrophobic behavior was reported, i.e., reaction rate increase

at positive polarization. This corresponds to increase of the catalyst work function that leads to decrease in the adsorption strength of electron acceptor adsorbates, i.e., oxygen, and strengthening of the adsorption bond of electron donor adsorbates, CH₄ [38,39].

Earlier EPOC studies on Pd for methane oxidation and for over 100 other catalytic systems, were carried out using continuous thin-film catalysts [40,41], characterized by high catalyst loading and low dispersion [42]. In the last decade, a strong emphasis has been made on the development and application of EPOC to nano-sized, highly-dispersed catalysts [43–50]. The use of nanostructured catalysts opens up the possibility of practical utilization of EPOC, and allows investigation of other similar phenomena in heterogeneous catalysis, i.e., metal-support interaction (MSI) and chemical promotion [51–56].

In the present work, we synthesized Ni_9Pd (Ni:Pd = 9:1 atomic ratio) nanoparticles using modified polyol method. The prepared Ni_9Pd NPs were deposited on YSZ solid-electrolyte and tested for methane complete oxidation under open-circuit and EPOC conditions, between 425 and 500 °C, and using various gas compositions. To the best of our knowledge, this is the first report on EPOC of bi-metallic nanoparticles with low noble metal content for complete methane oxidation.

2. Experimental

2.1. Synthesis of Ni₉Pd, Ni and Pd nanoparticles

Ni₉Pd nanoparticles (NPs) with Ni to Pd atomic ratio of 9-to-1 were synthesized using modified polyol synthesis method. To this end, 0.357 g of Nickel (II) chloride hexahydrate (Sigma Aldrich®) and 0.0296 g of palladium chloride (Fisher Scientific[®]) precursor salts were dissolved in 50 mL of ethylene glycol (Fisher scientific[®]) in a three-necked flask. The mixture was heated up to 100 °C and after 2 min at 100 °C, 1.7 mL of 0.1 M of hydrazine (50–60% purity - Sigma Aldrich[®]) was added to the mixture. Addition of hydrazine resulted in the formation of Ni-hydrazine complexes $[Ni (N_2H_4)_2]^{2+}$ (detected by the color change to blue) [57]. Then 4.5 mL of 0.1 M NaOH was injected to the reaction mixture that reduced [Ni $(N_2H_4)_2]^{2+}$ complexes and Pd²⁺, and lead to the formation of Ni₉Pd nanoparticles. The mixture was refluxed for additional 30 min to ensure complete reduction of precursor salts and then cooled to room temperature. The final Ni₉Pd nanoparticles were magnetic, which allowed their recovery from the solution using a ferrite ring permanent magnet. The solution was washed with ethanol, then centrifuged repeatedly with additional ethanol washes in between. The product was finally separated and dried in air.

Mono-metallic Ni NPs were synthesized using a procedure reported earlier in details [58], which follows the same aforementioned procedure minus the addition of Pd precursor. Monometallic Pd NPs were synthesized using 0.133 g of PdCl₂ dissolved in 25 mL of ethylene glycol and 0.8 M NaOH. The mixture was heated up to 160 °C and stirred for 3 h. The final colloidal solution was cooled down and washed several times with ethanol.

2.2. Catalyst characterization

The catalysts were examined by X-ray diffraction (XRD) using Rigaku ultima IV multipurpose diffractometer. The diffractometer was equipped with an X'Celerator detector with monochromatic CuK α radiation (λ = 1.5418 Å) at 40 kV and 44 mA. The scan was performed between 20 and 80 °20 with a step of 0.03°/s.

The particle crystallite size was estimated using Debye-Scherrer equation:

$$D = \frac{0.94\vartheta_{Cu}}{\beta_{1/2}\cos\theta} \tag{3}$$

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where ϑ_{Cu} is the X-ray wavelength, $\beta_{1/2}$ is the line broadening over the full width at half maximum (FWHM) in radians, and θ is the Bragg angle.

Structure and morphology characteristics of the different catalytic layers were found using double aberration-corrected Scanning Transmission Electron Microscopy (STEM) with FEI Titan 80-300 HB in High-Angle Annular Dark-Field (HAADF) mode. To gain insight into the elemental distribution, Energy Electron Loss Spectroscopy (EELS) data at very high spatial resolution was collected with a Gatan K2 direct detection camera. HAADF- Energy Dispersive X-ray Spectroscopy (EDS) mapping was performed using FEI Tecnai Osiris STEM equipped with a field-emission electron source and four silicon drift detectors at 200 keV. Overall, the spatial distribution of nickel-palladium that results in mapping of elements present in a sample is allowed due to correlation between the intensity of energy loss of at a given characteristic energy (for a particular element excited by the primary beam) with the number of atoms probed by the primary electron beam. Transmission Electron Microscopy (TEM) imaging for the nickel sample was obtained using JEOL 2100F TEM/STEM operating at 200 kV.

2.3. Electrochemical cell and reactor

A disk of 8 mol % Y_2O_3 -stabilized ZrO_2 (YSZ) (TOSOH[®]) solid electrolyte with 19 mm diameter and 1 mm thickness was formed following the procedure reported earlier [59]. 1.5 g of YSZ powder was mechanically pressed at 5000 psi and densified to above 95% by heating to 1000 °C (10 °C/min) and dwelling for 1 h, followed by heating with similar rate to 1500 °C and dwelling for 6 h [59].

Inert gold reference and counter electrodes were deposited on one side of the disk by applying thin gold paste coating (Gwent Group) of 0.2 and 1 cm² surface areas, respectively. This was followed by annealing in air at 500 °C. The catalyst-working electrode was deposited on the other side of the solid electrolyte disk (1 cm² surface area) opposing to the counter electrode. To this end, Ni₉Pd or mono-metallic Ni and Pd were dispersed in isopropanol and 10 μ L of a suspension were deposited at a time with intermediate drying at room temperature. The resulting total metal loading was 0.3 mg of Ni₉Pd on YSZ (0.3 mg in total of which 0.03 mg is Pd). The loading of monometallic Pd and Ni was 0.3 mg.

Catalytic measurements were carried out at atmospheric pressure in the single-chamber capsule reactor reported earlier [53,55]. The working electrode side of the electrolyte was pressed against a catalytically inert gold mesh (1 cm²) that served as a current collector, while the counter and reference electrodes were pressed directly against inert gold wires [58]. The inertness of gold mesh and electrodes was verified under reaction conditions. Two type K thermocouples (Omega[®]) were placed in vicinity of the electrochemical cell, one for temperature control and one for data acquisition.

2.4. Catalytic and electrochemical measurements

The reaction gases were oxygen (Linde, 99.99% O₂), methane (Linde, 99.99% CH₄), and helium (Linde, 99.997% He) as a carrier gas. The total flow rate was constant at 100 mL min⁻¹, unless otherwise stated. Gas composition was varied using MKS, 1259 C and 1261-C series flow meters. Non-dispersive infrared (NDIR) CO₂ gas analyzer (Horiba, VA-3000) and Mass Spectrometer (MS) (Ametek[®]) were used in series to analyze the concentration of CO₂ along with H₂O, CO, CH₄ and O₂. A potentiostat-galvanostat (Arbin Instruments[®], MSTAT) was connected to the electrodes to apply constant electric current or potential to the solid-electrolyte electrochemical cell.

3. Results and discussion

3.1. Physicochemical properties of bi-metallic Ni₉Pd and monometallic Ni and Pd nanoparticles

The XRD patterns of the as-prepared Ni₉Pd and mono-metallic Ni and Pd NPs catalysts are shown in Fig. 1. Both Pd and Ni have face-centered cubic (fcc) structure with characteristic diffraction peaks: (111), (200) and (220). In Ni₉Pd pattern, the (111) reflection peak of Pd appears at 40.5 $^{\circ}2\theta$ while that of Ni (111) at 44.4 °20. When compared to mono-metallic diffractograms, the (111) peaks of Pd and Ni are slightly shifted towards each other, i.e., Pd (111) is shifted to higher and Ni (111) is shifted to lower 20 suggesting formation of bi-phase structure between the two metals. Furthermore, Pd and Ni (200) and (220) crystallite peaks are shifted in the same manner. The summary of the 2θ peak position and full width at half maximum ($\beta_{1/2}$) is shown in Table 1. Using the background at 55 °20 and the FWHM of the corresponding (111) fcc peak, the crystallite size of Pd, in the bimetallic Ni₉Pd, was found at 4 nm while that of Ni was 5 nm showing equivalent crystallite sizes of the two metals. The crystallite sizes of mono-metallic Pd and Ni were 8 and 30 nm, respectively.

The morphology and particle size were examined using ADF/ STEM (Fig. 2a) for Ni₉Pd and TEM (Fig. 2b–c) for mono-metallic Ni and Pd. The particles of Ni₉Pd and Pd were spherical in shape with 10 nm average particle size for Ni₉Pd and 5 nm for monometallic Pd. Ni mono-metallic showed formation of spikes on its surface, adapting an urchin-like shape and 100–130 nm average particle size.

Further investigation of the structure and composition of Ni₉Pd was carried out using HAADF STEM-EDS and EELS (Fig. 3 and Fig. 4, respectively). In Fig. 3a, HAADF-STEM image shows the morphology of the sample. The overall EDS map of the mixture of Ni and Pd is shown in (b) while their corresponding elemental mapping is shown in (c) and (d). It can be seen in Fig. 3b the overall homogeneous mixing of both metals Ni and Pd in the catalyst (overlapping yellow color). In addition, more accurate high-resolution EELS mapping at 5 nm scale (Fig. 4) showed that Ni₉Pd has a core double-shell distribution with palladium-rich core surrounded with a Ni shell and on top of it a thin 3–4 nm layer of finely dispersed Pd. The Pd-rich core can be explained by the easier reduction of Pd during the NPs synthesis, if compared to Ni. In this case, the initially formed Pd clusters serve as seeds for Ni reduction and growth [60].

3.2. Open-circuit methane oxidation

The catalytic activity of Ni₉Pd for complete methane oxidation was investigated under open-circuit and compared to mono-



Fig. 1. XRD patterns of mono-metallic Ni, Pd and bi-metallic Ni₉Pd catalysts.

| Table 1 | | | | |
|--------------------------|--------------------------------------|--|--------------------------|------------------|
| The peak position and fu | ll width at half maximum (β_1 | /2) for Ni ₉ Pd bi-metallic | , and Pd and Ni mono-met | allic catalysts. |
| | D1 (4.4.4) | N: (1 1 1) | D1(200) | NI: (2.0 |

| Element | Pd (1 1 1) | Ni (1 1 1) | Pd (200) | Ni (200) | Pd (220) | Ni (2 2 0) |
|---|--------------|--------------|--------------|--------------|--------------|--------------|
| Ni ₉ Pd bi-metallic 2θ position (°) β _{1/2} (°) | 40.5 2.18 | 44.4 1.68 | N/A N/A | 51.5 2.83 | 68.3 1.74 | 76.3 2.48 |
| <i>Ni mono-metallic</i> 2θ position (°) β _{1/2} (°) | - | 44.6 1.5 | - | 51.9 0.6 | - | 76.5 0.8 |
| <i>Pd mono-metallic</i> 2θ position (°) β _{1/2} (°) | 40.1 1.1 | - | 46.5 1.76 | - | 68.2 2.2 | - |



Fig. 2. (a) HAADF/STEM of Ni9Pd and (b) TEM image of Pd NPs and (c) TEM images of Ni urchin-like NPs.

metallic Ni and Pd catalysts. Fig. 5a shows the higher open-circuit catalytic rate per gram of Pd (left axis) and gram of Ni (right axis) for Ni₉Pd compared to Pd and Ni mono-metallics. The higher mass activity of Ni₉Pd is due to the greater dispersion of small Pd clusters over Ni phase observed in the double shell-core structure (Fig. 4c). The outer highly dispersed Pd shell is characterized by the higher active surface area and better gas accessibility. Furthermore, an electronic interaction between Ni and Pd clusters cannot be ruled out, as the work function of bulk Pd and Ni is 5.1 eV and 5.3 eV, respectively [61] and could reach much higher values for Pd clusters or single atoms [62]. Monometallic Ni showed very low catalytic activity in this temperature range, which is in agreement with the literature, as much higher temperatures (>550 °C) are required for efficient methane oxidation on Ni [63]. Fig. 5b presents the variation in reaction rate as a function of reactants partial pressures for Ni₉Pd. For example, at P_{CH_4} = 17 kPa and P_{O_2} in the range of 0.5–3.5 kPa, P_{O_2} was the limiting variable and therefore, rate of reaction increased linearly with the increase of P_{O_2} . However, at P_{CH_4} = 2 kPa and where P_{O_2}/P_{CH_4} was close to stoichiometry, insignificant variation of reaction rate occurred as a function of P₀₂. This is in agreement with the Eley-Rideal mechanism, where methane weakly bonds on the strongly adsorbed oxygen on Pd sites when partial pressure of oxygen and methane are similar [38]. Whereas, a Langmuir-Hinshelwood mechanism was followed at lower P_{O_2}/P_{CH_4} ratio due to the more available sites for CH_4 adsorption directly on Pd [38].

3.3. Electrochemical promotion of methane oxidation

Fig. 6 shows the reaction rate of Ni₉Pd and Pd during a constant positive current application (+80 μ A) at stoichiometric ratio of P_{0,}/P_{CH4} = 2 at 450 °C. Contrary to Ni₉Pd and Pd NPs, mono-

metallic Ni did not show any response to the applied potential or current at any temperature or gas compositions of this study. This could be related to the low open circuit activity of Ni in this temperature range [63]. EPOC of mono-metallic Pd NPs for complete methane oxidation showed lower o.c. catalytic rate in comparison to that of Ni₉Pd and additionally a slower reaction rate increase with positive current application without reaching the steadystate value even after 2 h of polarization. This was explained by continuous activation of Pd by forming more active PdO_x surface as demonstrated in [64]. Upon the current interruption, the reaction rate slowly returned to its initial o.c. value for both Ni₉Pd and Pd indicating that the oxygen stored during positive polarization acted as a sacrificial promoters under open circuit. The time to return to the initial o.c. rate value was 30 min and 1 h for Ni₉Pd and Pd, respectively. The 10 times higher Λ value found for monometallic Pd shows that while the reaction rate per mass of catalyst is in the same range for both catalysts, the rate per mole of oxygen (O s^{-1}) differs noticeably, because Pd loading in the bimetallic catalyst is 10 times less than in monometallic Pd catalysts.

Fig. 7 shows the reaction rate response and corresponding current as a result of a constant positive potential application between the Ni₉Pd catalyst and the counter electrode at 425 °C. At the beginning of the experiment (t < 0.5 h), the open-circuit catalytic rate, r_o , was stable at a value of 1×10^{-8} mol O/s. When a constant potential $U_{WR} = 0.5$ V was applied, it caused an increase in the catalytic rate, reaching a new value of 1.92×10^{-8} mol O/s and resulting in a rate enhancement ratio, ρ of 1.92. The reaction rate increase is 21 times larger than the back-spillover supply of $O^{\delta-}$ onto the catalyst surface from the solid electrolyte [32]. According to EPOC mechanism, the presence of $O^{\delta-}$ species at the gas exposed catalyst surface and the resulting effective double-layer formation modifies the work function of the catalyst surface thus affecting



Fig. 3. HAADF STEM image of Ni₉Pd (a) and resulting EDS mapping of Ni (red) and Pd (green) in (b), (c) and (d). Scale bar is 60 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the binding strength of covalently bonded adsorbates [25,56,65,66]. In fuel-lean conditions, increasing catalyst potential and its corresponding work function causes a weakening of the binding strength of electron acceptor adsorbates, e.g., chemisorbed oxygen. This results in weakening of Pd-O bond strength and thus facilitating dissociative step of oxygen from the surface of Pd as reported earlier for Pd catalyst at 500 °C [30,43]. Once the potential application was interrupted, the catalytic rate slowly (over 0.75 h) decreased to its initial value showing that the observed effect is reversible.

Fig. 8 summarizes the rate enhancement ratio and apparent Faradaic efficiency of EPOC results shown in Fig. Sl. 3. Fig. 8a demonstrates that the enhancement ratio of the methane oxidation was related to the oxygen coverage on the catalyst surface indicating that less oxygen was adsorbed onto the catalyst sites and hence a partial palladium oxide reduction occurred. In addition, the increase in the surface potential from 0.25 to 0.5 V led to a greater increase in the closed-circuit catalytic rate. The ρ value as a function of partial pressure ratio was higher at 425 °C than at 450 °C as the catalyst is in an already more enhanced state at a higher temperature; therefore, the migration of $O^{\delta-}$ towards the surface has a less significant influence on the rate at 450 than at 425 °C. A similar trend is shown in Fig. 8b for the apparent Faradaic efficiency as a function of the partial pressure ratio and temperature. Furthermore, transient rate responses upon constant applied potential at 0.5 V at 475 and 500 $^\circ$ C are shown in Figs SI. 4 and 5.

It should be noted that electrochemical promotion of methane oxidation on Ni_9Pd was negligible in very lean fuel-conditions (not shown here). This is also supported by the literature where EPOC experiments were reported in stoichiometric or near stoichiometric conditions, due to the strong bonding of oxygen onto the Pd surface [36,38,43].

To further clarify the effect of oxygen partial pressure on the methane oxidation, we carried out EPOC experiments under fuelrich conditions. The partial pressure of CH₄ was kept constant at 10 kPa and that of oxygen was varied between 0.4 and 17 kPa. The EPOC transient experiments upon positive polarization are shown in Fig. SI. 6, while the enhancement ratio and apparent Faradaic efficiency are summarized in Fig. 9 as a function of P_{O_2}/P_{CH_4} ratio. At a very low P_{O_2}/P_{CH_4} ratio, the Faradaic efficiency and enhancement ratio were more significant due to the ease of CH₄ adsorption under a constant positive potential application. This is to show that the electrochemical promotion of the CH₄ adsorption is more significant in reduced conditions where more sights for CH₄ are available on PdO_x surface. These electropromotion results are in good agreement with the open circuit behaviour of Ni₉Pd



Fig. 4. HAADF STEM-EELS and element mapping showing (a) Pd at signal range: 364.3–468.0 eV, (b) Ni at signal range: 848.0–885.8 eV and (c) combined color coded map of Pd shown in the core (green areas) and Ni (red) with a further outer Pd shell of 3–4 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. (a) Light of curves of catalytic complete methane oxidation ($P_{CH_4} = 2$ kPa and $P_{O_2} = 4$ kPa) over Pd, Ni and Ni₉Pd catalysts (b) Effect of oxygen and methane partial pressure on catalytic rate of Ni₉Pd at 450 °C.

under various P_{O_2}/P_{CH_4} (Fig. 5b), where the higher open and closed circuit reaction rates were observed under stoichiometric and fuelrich conditions. At lower oxygen partial pressure, the partially oxidized PdO_x is more susceptible to positive current or potential application (work function increase), which destabilizes the oxide film forming the active PdO_x surface species. Under excess of oxygen the open circuit rate is low (Fig. 5b) and no EPOC was observed because Pd is fully oxidized forming a thermodynamically stable oxide film.

Fig. 10a shows the effect of increasing the positive potential on Ni₉Pd catalyst at a constant P_{O_2}/P_{CH_4} ratio (1/10) and T = 425 °C. The application of higher current or potential corresponds to a great work function increase in agreement with the potential-work function relationship under the action of promoters [21,25].

Fig. 10b shows the reaction rate increase, Δr , between opencircuit and closed-circuit values as a function of applied potential, represented by $O^{\delta-}$ flux (I/2F). The solid lines depict constant Faradaic efficiency, Λ lines. It can be seen that Faradaic efficiency was higher at lower applied potential, having a maximum value of 25 when 0.25 V was applied (i.e., 2.8 10^{-10} mol $O^{\delta-}$ s⁻¹).

Our results demonstrated that Ni_9Pd catalyst with core doubleshell structure could be efficiently electropromoted using anodic polarization. The Pd core NiPd shell structure with the presence of nm-thick layer of highly dispersed Pd clusters on the Ni shell resulted in an active and stable catalytic performance under open-circuit and EPOC conditions. Furthermore, this configuration allowed a faster and more stable electrochemical promotion of Ni₉-Pd compared to mono-metallic Pd (Fig. 6).



Fig. 6. Transient rate response of Pd and Ni₉Pd NPs to applied positive current, 80 μ A. Reaction conditions: T = 450 °C, P_{CH4} = 2 kPa and P_{O2} = 4 kPa, He balance.



Fig. 7. Transient rate response of Ni₉Pd NPs and corresponding current to a step change of an applied potential U_{WR} = 0.5 V; o.c.: open-circuit. Reaction conditions: T = 425 °C, P_{CH4} = 2 kPa and P₀₂ = 6 kPa, He balance.



Fig. 9. Faradaic efficiency and enhancement ratio corresponding to transient rate response of Ni₉Pd to a step change of an applied potential, U_{WR} = 0.25 and 0.5 V. Reaction conditions: T = 450 °C.P_{CH4} = 10 kPa, P₀₂/P_{CH4} is a variable.

4. Conclusion

Electrochemical promotion of Ni₉Pd nanoparticles with Pd core, Ni-Pd double-shell structure was investigated for complete methane oxidation reaction between 425 and 500 °C. The promotion of the catalytic activity of Ni₉Pd supported on YSZ solid electrolyte was achieved at positive polarization and outperformed the activity of mono-metallic Pd nanoparticles under open- and close-circuit conditions. Upon positive potential application between Ni₉Pd catalyst-electrode and the counter electrode, the electrophobic EPOC behavior resulted in a catalytic rate enhancement up to 240% with an apparent Faradaic efficiency of 25 at 425 °C. Variation of reactants composition showed that promotion was the highest under fuel-rich conditions compared to stoichiometric or fuel-lean conditions. The double shell-core structure with highly dispersed Pd clusters on the outer shell is responsible for the high activity of Ni₉Pd catalyst under open- and closedcircuit conditions due to the high active surface area of Pd clusters as well as likely electronic interaction between Pd and Ni. Our work demonstrates that fabrication of well-defined bi-metallic nanoparticles with low noble metal content, as well as controlled surface structure and composition is of great importance for practical advancement of EPOC. Application of Ni₉Pd nanoparticles for



Fig. 8. Effect of oxygen partial pressure on (a) the enhancement ratio and (b) Faradaic efficiency at 425 and 450 °C; U_{WR} = 0.25 and 0.5 V.P_{CHa} = 2 kPa.



Fig. 10. (a) Reaction rate response to a constant positive potential application on Ni₉Pd at 425 °C for P_{CHa} = 10 kPa, P_{O2} = 1 kPa; (b) The reaction rate increase, Δr, as a function of applied potential, represented by $O^{\delta-}$ flux (I/2F).

complete methane oxidation has several advantages: the low noble metal content, and fast and stable EPOC. All this makes electrochemically activated Ni₉Pd catalyst potentially attractive for utilization in gas exhaust treatment devices.

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Appendix A. Supplementary material

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