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Influence of Pd and Au on electrochemical valorization of glycerol over Ni-rich surfaces



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ABSTRACT

Herein we synthesized bi-metallic Pd@Ni and Au@Ni core-shell-like nanoparticles (NPs) for glycerol electrooxidation reaction (GEOR) in alkaline media. The morphological, structural and surface properties of the NPs were evaluated using a range of physicochemical techniques. The catalytic activity and stability were studied using the three-electrode electrochemical cell and 25 cm²- continuous electrolysis cell. Among different atomic ratios, $Ni_{80}Pd_{20}$ and $Ni_{90}Au_{10}$ nanoparticles showed the highest current densities which are ~4.5 and 4.2 times higher than spherical Ni, respectively. The addition of Pd and Au (<20 at.%) to Ni nanoparticles led to a remarkable glycerate selectivity of ~73.1% and 65.7% for $Ni_{80}Pd_{20}$ and $Ni_{90}Au_{10}$ catalysts at 1.3 V and 50 °C, respectively. Notably, after 6 h of electrolysis Pd@Ni and Au@Ni tend to suppress the C-C bond cleavage, compared to Ni at any applied potentials and temperatures. The DFT calculations predicted that the addition of Pd or Au to Ni reduces the work function of M@Ni NPs, which strengthens the OH adsorption and enhances the removal of GEOR intermediates.

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1. Introduction

Glycerol electrooxidation reaction (GEOR) is a viable and efficient way of converting an excess of glycerol, a by-product of biodiesel production [1–3], to value added chemicals [4–6]. GEOR was proposed over two decades ago, however there are still several questions that remain to be answered before this process could see practical application. The central issue is a type of electrocatalyst and the nature of the active sites that in turn dictate the catalytic activity and selectivity towards desired products [4]. There are several possible reaction pathways for the partial electrooxidation of glycerol, which result in various products: glycerate, tartronate, hydroxypyruvate, glycolate, oxalate, dihydroxyacetone, mesoxalate and formate [7–10], therefore development of efficient and stable electrocatalysts with high selectivity to the preferred products has been a central topic of GEOR research in recent years [5].

Several noble platinum-, palladium- and gold-based catalysts have been developed [11–15]. Results showed that gold outperforms the other noble metals in alkaline media due to its relatively

* Corresponding author. E-mail address: elena.baranova@uottawa.ca (E.A. Baranova). high anti-poisoning capabilities and large capacity to adsorb hydroxyl ions, which promote the oxidation reaction [16]. *Maumau et al.* tested Au/C which showed to have high current density and anti-poisoning ability to surface oxides compared to Pd/C [17]. Similarly, gold disk electrodes exhibited nine times higher current density than palladium disks [18]. Regarding selectivity, the main products formed on Pd, Pt and Au have been shown to be glycerate ions, mesoxalate and/or tartronate with a unique selectivity to hydroxypyruvate ion on gold [19,20]. In addition, AuPt alloy showed a selectivity to lactic acid (73%), which is a valuable product used in several industries [8].

Among the non-noble metals, nickel is the most common metal used in electrochemical technologies, e.g., rechargeable batteries, fuel cells, sensors, alkaline water electrolysis and supercapacitors, [21–23] due to its high current densities and good stability in alkaline media [24]. Several recent studies explored Ni and Ni-based electrocatalysts for GEOR [24–29]. It is proposed that the region of nickel oxy-hydroxide formation (NiOOH) at (1.4 V vs RHE) is the active phase for GEOR on Ni surfaces [24–26]. Oliveira et al. reported that main products on carbon supported Ni, NiCo and NiFe are formate with minor amounts of glycolate, glycerate, tar-tronate, and oxalate [26]. In our recent report, we synthesized Ni-Bi double-shell/core structure that showed a 2-fold enhanced





GEOR activity when compared to monometallic Ni [28]. The addition of 10 atomic (at.) % of Bi improved the formation of C₃ products by suppressing the C–C bond cleavage. In another study, we reported that Ni-Pd double-shell/core nanoparticles (NPs) of various composition showed higher electrocatalytic activity towards GEOR than monometallic Ni due to a synergistic effect between the two metals, however, the reaction pathway and selectivity were similar to that of monometallic Ni [29]. For carbon supported Ni_xM_{1-x} (M = Bi, Pd and Au) nanomaterials with different atomic ratios, generated 100% selectivity towards formate with 100% conversion at +1.55 V [27]. This work was a pioneer in combining glycerol and CO₂ valorization using Ni-rich materials.

Theoretical methods for studying properties of bimetallic NPs have become an important tool for predicting reactivity, stability and magnetic properties of nano clusters. Several authors studied the structural properties, stability, anisotropy, strain, mixing energies, magnetic properties and chemical order of NPs formed by metals of the groups 10 and 11 [30–36]. These NPs present a size-dependent evolution of their structure and properties, where the geometric shape and the energetic stability of NP could drastically change with size [30]. Also, the accumulation of strain at the atomic level and its subsequent release can be responsible for the symmetry breaking that make possible the different size- and composition-dependent transitions between the core@shell arrangements [31].

Zhu et al. investigated the structural and electronic properties of the icosahedral $Pd_{55-n}Ni_n$ (n = 0–55) clusters using DFT [37]. The authors found that the core-shell $Ni_{13}@Pd_{42}$ cluster is the most stable structure. The electronic property analysis revealed that the interaction between Pd-4d and Ni-3d orbitals makes the main contribution and a strong d–d self-interaction among the 3d orbitals of the Ni atoms. They also found that with an increasing number of Ni atoms, the d-band center of the surface Pd atoms shift away from the Fermi level, while the root mean squared d-band width broadens. This feature is also observed in the partial density of states (DOS) of the Pd surface atoms. The charges are partially transferred from Pd to Ni in the bimetallic cluster and partially from Ni atoms on the top sites to Ni atoms in the core.

In a recent publication, the impact of oxygen traces during TEM measurements on the phase transition from Ni-Au to Au-Ni coreshell clusters were investigated [38]. The combined theoretical and experimental approach showed that in the presence of trace oxygen, an Au-Ni core-shell system becomes thermodynamically preferred at elevated temperatures, even before a full oxidation of the reactive metal takes place. The diffusion of Ni to the surface is catalyzed by the presence of oxygen. Therefore, for bimetallic nanoparticles in this size regime, the gas adsorption onto the protective noble metal shell can destabilize the core-shell structure by an enhancement of intermetallic diffusion.

Herein, we synthesize bimetallic nickel rich catalysts Ni_xAu_{1-x} [x = 100, 98, 95, and 90 at.%] and Ni_xPd_{1-x} [x = 100, 95, 90 and 80 at.%] catalysts using a sodium borohydride method, which could be easily scaled up. Firstly, the fabricated nanoparticles were characterized in detail using transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron microscopy (XPS), energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS). In addition, the electrochemical performance was evaluated by cyclic voltammetry (CV), chronoamperometry (CA), linear sweep voltammetry (LSV) and durability test (cycling for 300 cycles) in alkaline media. Product distributions of GEOR were also analyzed by HPLC in a membranless continuous electrolysis cell (25 cm²) at different applied potentials and temperatures. Finally, to shed light on the experimental observations and elucidate the interaction between Ni and the second metal (Pd or Au), a series of DFT calculations on smaller, finite model systems have been carried out. To this end, we calculated the excess energy, electronic structure, d band center, work function (WF) and strain between core-shell layers and corelated these results with the experimental findings.

2. Methodology section

2.1. Material synthesis

The Ni_xAu_{1-x} (x = 100, 98, 95, and 90 at.%) and Ni_xPd_{1-x} (x = 100, 95, 90 and 80 at.%) catalysts were synthesized via wet chemical synthesis. The detailed methodology was reported in our previous work [29]. Briefly, the metal precursor salts nickel (II) chloride hexahydrate (ALDRICH Chemistry, 99.999% purity), gold (III) chloride (ACROS Organics, 99% purity) and palladium (II) chloride (ALDRICH Chemistry, \geq 99.9% purity) were dissolved in ethanol solvent in a controlled weight percentage ratio. After complete dissolution, the sodium borohydride powder (ACROS Organics, 98+% purity), which is the reducing agent, was added to the mixture. Finally, the samples were centrifuged and freeze dried.

2.2. Physicochemical and electrochemical characterizations

Various physicochemical metohods (TEM, SAED, XRD, XPS, HAADF, EDS, EELS) were implemented. In addition, different electrochemical tests (CV, LSV, CA) were conducted. The detailed procedures were explained elsewhere [29]. All potentials were measured with respect to mercury–mercury oxide (Hg/HgO) (Koslow Scientific) but reported versus the reversible hydrogen electrode ($E_{RHE} = E_{Hg/HgO} + 0.855$ vs RHE), unless otherwise stated.

2.3. Chromatographic analysis of products

The continuous electrolysis cell (25 cm²) was used to study the catalyst performance and product distributions during GEOR [28]. The HPLC measurement and standard calibration details were previously reported along with a sample calculation [28].

2.4. Theoretical modeling and calculations

To develop several finite size models to complement experimental characterization we perform DFT calculations using the VASP code [39]. The calculations are spin polarized since most systems have magnetic properties. According to the experimental results for the NPs, we focus on icosahedral and decahedral clusters. We studied the 13- and 55-atoms icosahedral (Ih₁₃ and Ih₅₅, respectively) and 54-atoms decahedral (Dh₅₄) nanoparticles. The 13 atoms systems were studied in order to validate our theoretical methodology. These results are discussed in the supporting information and compared with other experimental and theoretical findings from literature. The 55-atoms icosahedral NP serves as a model system resembling the experimental finding, with an almost spherical shape and (111) faces terminations. Also, the NPs with icosahedral structure have good stability [34,40-42]. From the point of view of surface energy, this structure is a highly strained non-crystalline one with a quasi-spherical shape and closepacked surface, which optimizes the surface energy well. In addition, the icosahedral NPs are obtained by packing together twenty tetrahedrons sharing a common vertex. This packing causes the high internal strain of the structure and the efficient minimization of the surface energy, which favored this structure at small sizes [34,40,41]. The decahedral structure also has (111) faces termination. In both systems the composition of bimetallic NP is in the range of that synthetized experimentally. More information on the schematic models is given in Fig. S1 in SI. The Ih₁₃-, Dh₅₄and Ih₅₅-NPs are configured as core_m@shell_n systems, i.e., M_m@Ni_n (as mentioned before Ni_xM_{1-x}) particles (M = Au and Pd), where "m" is the number of M-atoms in the core and "n" is the number of Ni-atoms in the shell. In this work, we study the Ih_{13} - $M_1@Ni_{12}$, Ih_{55} - $M_1@Ni_{54}$, Ih_{55} - $M_{13}@Ni_{42}$ and Dh_{54} - $M_7@Ni_{47}$ systems.

3. Results and discussion

3.1. Physicochemical characterization of Ni_xM_{1-x} NPs

The morphological features of as prepared Ni_xM_{1-x} (M = Pd and Au) NPs were investigated by TEM. Fig. 1a and d shows representative micrographs of Ni₉₀Pd₁₀ and Ni₉₀Au₁₀, nanoparticles, respectively. TEM reveals almost spherical nanosized particles possessing irregular aggregate shapes, with average particles sizes in the range of 3–5 nm. For these materials, the high rates of agglomeration could be elucidated by the strong attractive magnetic force between colloids during the synthesis procedure [29]. Nevertheless, the presence of the second metal Pd or Au, have approximately halved the average catalyst size compared to our previously reported spherical Ni (9.2 \pm 2.4 nm) [28]. This reason is due to that second metals acted as a heterogeneous nucleation agent preventing Ni from growing, resulting in a smaller crystallite size compared to monometallic Ni.

Moreover, XRD measurements were conducted to identify the crystal structure of nanosized Ni₉₀Pd₁₀ and Ni₉₀Au₁₀ catalysts. As shown in Fig. 1b and e, the peaks showed distinct face-centered cubic (fcc) structure of Pd(111) and Au(111), respectively, with the presence of Ni(111) and β -Ni(OH)₂(100). The corresponding selected area electron diffraction (SAED) pattern (Fig. 1c and f) revealed asset of full rings, indicating that the bi-metallic nanoparticles have high polycrystalline nature, which is in agreement with our XRD data. However, the diffraction rings were not indexed due to close proximity of Ni to Pd and Au.

To gain additional information about the surface electronic state and chemical composition of Ni_xM_{1-x} catalysts, Fig. 2a-c depict the XPS spectra of Pd 3d and Au 4f core level regions, respectively, along with Ni 2p XPS spectrum. Monometallic Ni shows Ni $2p_{3/2}$ and Ni $2p_{1/2}$ peaks with binding energies at 856.1 and 873.9 eV, respectively, and two satellite peaks positioned at 861.9 and 880.0 eV. The position of the peaks corresponds to the formation of Ni(OH)₂ phase with the 17.8 eV binding energy distance [43,44]. For $Ni_{90}Pd_{10}$ and $Ni_{90}Au_{10}$ samples, one can observe similar peaks corresponding to Ni 2p with a higher shift of 0.5 eV compared to Ni, which indicates that the chemical environment of Ni²⁺ is affected. Fig. 2b, the Pd 3d spectrum is positioned between 331 and 345 eV with two doublets Pd 3d_{5/2} (334.8 eV) and Pd $3d_{3/2}$ (340.1 eV). The peaks position and the full width at half maximum (FWHM \approx 1.49 ± 0.04 eV) of the peaks confirm the presence of Pd atoms in the metallic state (Pd (0)) with the 5.3 eV binding energy distance [45,46]. In Fig. 2c, the two XPS peaks located at binding energies of 83.4 and 87.1 eV (spinorbital splitting of 3.7 eV and FWHM \approx 1.31 ± 0.07 eV) were attributed to Au $4f_{7/2}$ and Au $4f_{5/2}$, respectively, these values are in good correlation with the reported values for pure metal gold (Au(0))[45.47].

The spatial distributions of Pd and Au elements in Ni-rich NPs were characterized by the STEM-energy dispersive spectroscopy (EDS) mapping as depicted in Fig. 3a and b, respectively. The Z-contrast images illustrate that Ni (red) is uniformly distributed in the selected area. However, Pd and Au (green) are present in a large cluster in more specific area of the nanosized NPs. The EDS spectra are also in good correlation with the elemental composition of Ni₉₀Pd₁₀ and Ni₉₀Au₁₀. The physicochemical characterizations of other samples (Ni₈₀Pd₂₀ and Ni₉₅Au₅) are illustrated in the supporting information (Figs. S2 and S3).

Furthermore, the chemical microstructures of $Ni_{1-x}M_x$ surfaces were also mapped using STEM-EELS analysis. Fig. 3c and d illus-



Fig. 1. Morphology and structure characterizations of Ni₉₀Pd₁₀ and Ni₉₀Au₁₀ nanostructures (a,d) TEM image, (b,e) XRD patterns and (c,f) SAED patterns, respectively.



Fig. 2. High resolution XPS spectra for (a) Ni 2p (b) Pd 3d and (c) Au 4f.

trate the elemental distribution of (Ni $L_{2,3}$ and Pd–M_{4,5}) and (Ni $L_{2,3}$ and Au–M_{4,5}) within the Ni₉₀Pd₁₀ and Ni₉₀Au₁₀ NPs, respectively, which were extracted from different signals centered at ~855, 400 and 2200 eV for Ni $L_{2,3}$, Pd–M_{4,5} and Au–M_{4,5}, (Fig. S4 in ESI). The corresponding STEM–EELS map of Ni-M clearly shows that Pd and Au (green) ions are mostly located in the core region and non-uniform thin layer of Ni (red) ions are segregated on the surface forming a shell. This indicates the formation of M-core@Ni shell-like structures, with Au and Pd mostly present in the core of NPs indicating that both Au and Pd served as seeds during the NPs synthesis [29].

3.2. Glycerol electrooxidation on Ni_xM_{1-x} NPs

Fig. 4 shows cyclic voltammograms (CVs) of Ni_xPd_{1-x} (x = 100, 95, 90 and 80 at. %) and Ni_xAu_{1-x} (x = 100, 98, 95 and 90 at. %) catalysts in a N₂-purged 1 M KOH solution at 50 mV s⁻¹. The current densities of unsupported Ni_xM_{1-x} were normalized per mass of nickel, to avoid uncertainties involved in calculation of the electrochemical active surface areas (ECSA) of Ni-based materials [27]. The comparison of current densities per the geometric area (0.196 cm²) is given in Fig. S5a-b in ESI.

The CVs in the absence of glycerol were consistent with voltammogram profiles reported in the literature for Ni-based catalysts [24–27]. For monometallic Ni, the anodic peak (~1.44 V) and the cathodic peak (~1.18 V) correspond to the surface redox process of β -NiOOH/ β -Ni(OH)₂ [28]. For Ni₈₀Pd₂₀, a peak in the cathodic region centered at ~0.52 V (Fig. 4a inset) represents the reduction of PdO active sites available on the surface [19,29], whereas for $Ni_{95}Pd_5$ and $Ni_{90}Pd_{10}$, this peak is negligible, demonstrating Pd is mostly segregate in the core. Similarly, no reduction peak of quasi-2D oxide state of Au was observed as shown in Fig. 4b [48]. Addition of Pd and Au enhanced the current density of the Ni^{2+}/Ni^{3+} peak.

It can be noted that the Ni₈₀Pd₂₀ and Ni₉₀Au₁₀ catalysts have higher Ni^{II}/Ni^{III} redox peak (~3 x) followed by a more reversible redox process compared to monometallic Ni as shown in Fig. 4. The reason for the low current density of pure Ni could be its low conductivity, as it is mostly present as Ni oxide [49]. The presence of palladium and gold improved the conductivity, as well as the oxygen evolution reaction (OER). The OER current growth was initiated at ~1.56 V vs. RHE for Ni compared to ~1.52 V for Ni₈₀Pd₂₀ and Ni₉₀Au₁₀. The improved conductivity, as well as the smaller particle size of the bimetallic NPs, i.e., larger active surface area, could be responsible for the observed effect.

Cyclic voltammograms of unsupported Ni_xM_{1-x} catalysts in the presence of glycerol is shown in Fig. 5 and Fig. S5 in ESI. Adding some Pd or Au increases the activity, but further increasing the amount of Pd or Au does not seem to make much difference, no actual difference in the onset potential with further increase in the content of Pd or Au can be seen. For the set of catalysts studied, Ni₈₀Pd₂₀ and Ni₉₀Au₁₀ showed the highest mass current densities of 543 A g_{Ni}^{-1} and 504 A g_{Ni}^{-1} , respectively compared to 122.4 A g_{Ni}^{-1} for Ni at 1.58 V vs. RHE (Fig. 5a and b). The onset potential of GEOR is negatively shifted by ~100 mV and 50 mV for Ni₈₀Pd₂₀ and Ni₉₀-Au₁₀ compared to spherical Ni, indicating an enhancement in oxidation kinetics. Moreover, these current densities are higher than the ones reported for Ni_xPd_{1-x} [29].



Fig. 3. Dark Field-STEM image, EDS elemental spectrum and mapping of (a) Ni and Pd elements of Ni₉₀Pd₁₀ and (b) Ni and Au elements of Ni₉₀Au₁₀. HAADF-STEM images and EELS Mapping of (c) Ni₉₀Pd₁₀ and (d) Ni₉₀Au₁₀ catalysts.



Fig. 4. Cyclic voltammograms of Ni-based catalysts (a) NixPd_{1-x} and (b) NixAu_{1-x} performed in 1 M KOH electrolyte at scan rate of 50 mV s⁻¹ (10th stable cycle).

For Ni₈₀Pd₂₀ synthesized at high temperature using hydrazine as reducing agent showed a ~2.5x lower mass activity compared to our recent Ni₈₀Pd₂₀ catalyst fabricated using sodium borohydride method. Addition of Pd and Au promoted the activity of Ni much more than bismuth [28]. For NiBi electrocatalysts, the maximum current density obtained over Ni₉₀Bi₁₀ was 436.5 A g_{N1}^{-1} , at 1.58 V vs. Hg/HgO which is lower than the data obtained in this report. For higher Pd and Au content, we observed an additional oxidation peak centered at ~-0.1 V vs. Hg/HgO which attributed to GEOR on Pd sites for Ni₈₀Pd₂₀ (Fig. 5a, inset) [29]. Whereas, two additional oxidation peaks appeared at \sim 0.12 V vs. Hg/HgO ascribed to GEOR on Au sites, demonstrating that gold by itself has much lower overpotential compared to Ni [48]. Fig. 5b, inset illustrates more intense peaks with higher Au content.

The increase in activity with addition of Pd and Au is further observed in the linear sweep voltammetry (LSV) test in Fig. S5 c and d in ESI. Clearly, bimetallic catalysts have lower onset potentials and higher mass current densities than on monometallic Ni. The durability tests of the unsupported Ni_xM_{1-x} catalysts were attained by running 300 consecutive CV cycles in 1 M



Fig. 5. Cyclic voltammograms of Ni-based catalysts (a) Ni_xPd_{1-x} and (b) Ni_xAu_{1-x} in 1 M KOH + 0.1 M glycerol solution at scan rate of 50 mV s⁻¹ (10th stable cycle). Normalized current density percentage vs CV cycles of (c) Ni_xPd_{1-x} and (d) Ni_xAu_{1-x} catalysts at 1.58 V vs. RHE.

KOH + 0.1 M glycerol. After 300 cycles in (Fig. 5c and d), $Ni_{80}Pd_{20}$ and $Ni_{90}Au_{10}$ exhibited the highest activity and retained ~51% of their initial current density compared to ~22% for Ni. The drop of activity can be explained by mechanical degradation of the catalysts and/or surface blocking by intermediates. Based on the electrochemical analysis, we conclude that the $M_{1-x}Ni_x$ core-shell-like structure displayed superior GEOR stability and activity performance than monometallic Ni. This could be explained by improved conductivity of bimetallic NPs, their smaller particle size as shown by TEM and possible synergetic effect between two metals as will be discussed in the following sections.

3.3. Electrolysis experiments and product distribution

The best performing Ni₈₀Pd₂₀ and Ni₉₀Au₁₀, as well as Ni electrocatalysts were further investigated in the 25 cm² membraneless continuous electrolysis cell (flow rate = 1.6 mL s^{-1}). The electrolytic tests were carried out at various applied potentials of 1.3, 1.4 and 1.55 V, temperature ((R.T) and 50 °C) and two KOH concentrations of 0.1 and 1 M in 0.1 M glycerol. The resulting cell current during 6 h experiment is reported in Fig. S6 in ESI. The quantitative analysis of products was carried out using HPLC analysis by collecting 5 sample solution 0.6 mL of the electrolyte solution in 30 min, 1 h. 2 h. 3 h and 6 h. The comparison in glycerol conversions and product distributions of the catalysts are shown in Figs. 6 and 7 and S7-S10 in supporting information. The calibration curves for the C_3 (glycerate, tartronate, and lactate), C_2 (glycolate and oxalate) and C₁ (formate) products were reported previously [28]. According to the HPLC results, the primary products are glyceric (GLA) and formic acid (FA) while, the secondary products are tartronic (TA), lactic (LA), glycolic (GA) and oxalic (OX) acids.

In Fig. 6a–f. all catalysts show the same trend where the application of the low potential (1.3 V) resulted in the highest selectivity towards GLA and the lowest glycerol conversion (<14%). A temperature increase resulted in higher selectivity to GLA and consequently less FA production. These trends are consistent with our previous results for Ni₉₀Bi₁₀ [28]. Noticeably, the addition of Pd and Au reduced the extent of the decrease in GLA selectivity when applying higher potentials, the glyceric acid production in Ni, Ni₈₀-Pd₂₀ and Ni₉₀Au₁₀ decreases by ~2.4x, 1.3x, and 1.5x, respectively (Fig. 6a, c and e). The production of C₃ products especially glycerate is enhanced over the bi-metallic catalysts. Specifically, Ni₈₀Pd₂₀ achieved the highest GLA selectivity (73.02%) at 1.3 V and 50 °C (Fig. 6c), which represents the highest $C_3/(C_1 + C_2)$ achieved with Ni-rich catalysts to date [25-29]. Tartronic acid production, a high-value added product [50], is seven times higher over bimetallic NiPd and NiAu catalysts compared to monometallic Ni at 1.3 V and R.T. The selectivity change on Ni₈₀Pd₂₀ and Ni₉₀Au₁₀ could be due to the lower particle size of the bimetallic catalysts compared to monometallic Ni. [51,52]. Because the bimetallic catalysts have less of the electropositive Ni sites and thus less ability to C--C bond cleavage, this could explain the selectivity change [51]. Furthermore, $Ni_{90}Au_{10}$ has the highest tendency to produce LA (~3x) and GA (~2x) compared to Ni at 1.4 V and R.T (Fig. 6e). The fact that the addition of 10 at. % of Au to Ni-rich catalysts induced the production of lactate, indicates that Au increases the oxidative dehydration capacity of the catalyst favoring the reaction pathway leading to LA [8]. Also, the addition of gold modifies the electronic configurations of Ni resulting in different reaction pathways that led to partially oxidized intermediates such as TA and GA [51].

It was previously noticed that time has a vital role on product distributions [28]. After 6 h of continuous electrolysis, we observed



Fig. 6. Product distributions and glycerol conversion (dashed line) under different applied potentials and temperatures over the (a,b) Ni, (c,d) Pd₂₀Ni₈₀ and (e,f) Au₁₀Ni₉₀ in a 1 M KOH + 0.1 M glycerol. The left-hand figures illustrate product distributions after 30 min, while the right-hand illustrates products after 6 h Gray: formate; Yellow: lactate; Navy: glycolate; Dark Cyan: glycerate; Wine: tartronate and Violet: oxalate. The red shaded border represents temperature at 50 °C.

that GLA concentration dropped gradually to FA and glycerol conversion increased progressively as shown in Fig. 6 b,d,f and S7-S9 in ESI. On the other hand, Ni₈₀Pd₂₀ and Ni₉₀Au₁₀ catalysts produced less C₁ products after 6 h of electrolysis, compared to Ni. By applying a moderate potential of 1.4 V at 50 °C, the selectivity to formate is much higher on monometallic Ni (74.5%) compared to Ni-Pd (42.6%) and Ni-Au (40.3%). Additionally, at higher potential of 1.55 V, Ni₈₀Pd₂₀ had the highest selectivity of oxalic acid (6.9%) at 50 °C as illustrated in Fig. 6d. This observation indicates that the addition of a \leq 20 at. % of Pd and Au prompts the C₃ selectivity and hinders the further oxidation of GLA to FA.

The effect of 0.1 M KOH concentration on product distributions of $Ni_{80}Pd_{20}$ and $Ni_{90}Pd_{10}$ was investigated at 1.4 V as shown in Fig. 7a–d and S10. After 6 h of electrolysis, the glycerate production is reduced by (3.72x and 2.4x) in 1 M KOH vs. (1.6x and 1.23x) at 0.1 M KOH for $Ni_{80}Pd_{20}$ and $Ni_{90}Au_{10}$, respectively at room temperature. Similar trend is observed at higher temperatures. Based on the HPLC results, the proposed reaction pathway on Ni, NiPd and NiAu catalysts for GEOR is initially oxidized by the primary alcohol electrooxidation (glyceraldehyde), which is in good agreement with our previous study [28,29]. Further oxidation is either metal-catalyzed to produce GLA, TA, GA, OX, FA and carbonate or



Fig. 7. Product distributions and glycerol conversion at 1.4 V over the (a,b) Ni₈₀Pd₂₀ and (c,d) Ni₉₀Au₁₀ in a 0.1/1 M KOH + 0.1 M glycerol. The left-hand figures illustrate product distributions after 30 min, while the right-hand illustrates products after 6 h. The red shaded border represents temperature at 50 °C.

base-catalyzed dehydration forming lactate after Cannizzaro rearrangement [8].

In summary, addition of small amounts of Pd and Au impacts the selectivity by hindering the GLA oxidation to FA compared to the monometallic Ni, leading to higher selectivity to C_3 products at different applied potentials and temperatures. In addition, lower KOH concentration further enhances the hindering of C—C bond cleavage, leading to higher C_3 products after 6 h of continuous electrolysis.

To understand the exceptional GEOR performance of the core/ shell-like structured Pd/Ni and Au/Ni nanocatalysts, we performed DFT studies on Ih_{13} - $M_1@Ni_{12}$, Ih_{55} - $M_1@Ni_{54}$, Ih_{55} - $M_{13}@Ni_{42}$ and Dh_{54} - $M_7@Ni_{47}$ systems to calculate strain between core-shell layers, excess energy, electronic structure, d-band center and work function (WF).

3.4. Theoretical results

3.4.1. Stability and geometrical analysis

In order to analyze the results at varying composition, we calculate the normalized excess energy E* (equation 2 in ESI). The excess energy values for the considered systems shown in Fig. 8. As expected, all pure NPs have 0 eV. For the Ih₁₃ systems, the more stable configurations are Au₁@Ni₁Au₁₁ and Ni₁@Pd₁Ni₁₁. The configurations of Pd₁@Ni₁₂, Pd₁@Pd₁Ni₁₁, Ni₁@Pd₁₂ and Pd₁@Ni₁₂ present some morphological instability, although this does not mean that the cores have unstable configurations. The NPs have locally stable minima, whose energy is however much higher than the energy of the optimal configurations. These morphologies do not persist as the lowest-energy morphology when the proportion of core atoms increases in the nanoparticle, i.e., the term instability is referred to the overall core morphology and not to the local minimum corresponding to the centered core [31]. In the case of Ih_{55} -and Dh_{54} -NPs, the $Ni_1@Au_1Ni_{11}@Ni_{42}$ (Layer1@Layer2@Layer3 - Fig. S1) and Pd₁₃@Ni₄₂ systems were the more stable, respectively. The configurations $Au_{13}@Ni_{42}$ and $Au_7@Ni_{47}$ also present morphological instability.

The morphological instability has a physical origin that is related to strain release. In Fig. 9 optimized structures of the Ih₁₃, Dh₅₄ and Ih₅₅ NPs are shown. It can be seen that the Au@Ni icosahedral systems have the most important strain percentage (e Layer $_{\#}$, # = 2, 3), which is consistent with a strong structural deformation and the formation of mixed shell systems (the equation for strain (Eq. 4) is presented in ESI). This is consequence of the mismatch between the metal atomic radii. Also, in the system strain is reducing when the Ni shell diameter is higher than that of the Au core. For the Pd@Ni icosahedral NP we found less strain and therefore less structural deformation, which is consistent with a similar atomic radius of these metals. Despite this, the presence of strain and the fact of the mixed shell system have negative excess energy indicate that the Pd could segregate to the shell, but in a less amount that in the case of the NP with Au in the core. In the decahedral NPs the strain values are smaller and they have less geometrical distortion, as a consequence of more open structure. These results agree with the range of stable composition described in the STEM-EELS analysis (Fig. 3c and d) and CVs in 1 M KOH (Fig. 4).

3.4.2. Electronic structure

Regarding electronic structure, the d-band PDOS curves for icosahedral and decahedral systems are shown in Figs. 10 and 11. It can be seen that all systems are metallic. Also, with the exception of Au monometallic NP (see Figs. 10e and 11e), the spin



Fig. 8. Excess energy values of the N_nM_{1-n} NPs for (a,b) the 13-atoms icosahedral systems (purple) and (c,d) 55-atoms icosahedral systems (green) and 54-atoms decahedral systems (red).



Fig. 9. Optimized structures for theoretical core@shell nanoparticles. The labels above the NP system correspond to the estimated composition percentage of each metal.

up and spin down contributions are shifted and are asymmetrical which is consistent with a magnetic behavior.

The large magnetic moment value in the bare Ni_{55} icosahedral system (47.7 $\mu_B)$, suffer a slightly decrease when the central atom



Fig. 10. Curves of d-band PDOS for the 55-atoms icosahedral systems. The blue and red lines indicate the spin up and spin down contributions, respectively. The black line corresponds to the total d-band curve. Schematic of the mono and bimetallic systems.

if substituted by an Au- or Pd-atom. When all the core atoms are replaced by Au or Pd atoms (i.e. the 13th central atoms in the core) the magnetic moment decreases about 5.7 μ_B or 4.3 μ_B , respectively as illustrated in Fig. 10c, e, g, i and k. In addition, the Pd₅₅ NP has the smallest magnetic moment of the icosahedral systems (Fig. 10i). The decahedral systems show similar behavior (see Fig. 11). The magnetic moment values for the monometallic systems agree with those reported by Wang et al. [53,54] and Yang et al. [55]. The d-band center (ϵ_d) is an important factor for studying the systems reactivity, for this reason we calculate the values for the monometallic and bimetallic NP using Equation 5 in ESI.

Generally, in metal particles we have charge transfer (or redistribution), which further promotes Coulomb attraction (electrostatic force) between the inner-core atoms and surface-shell atoms. Thus, charge transfer is beneficial for stabilizing the bimetallic core-shell particles. In addition, the charge transfer may further induce the significant reorganization in the electronic structure. This may in turn lead to different chemical activities for different core-shell particles. For that matter, identification of simple reactivity descriptors from complex electronic properties of materials becomes tremendously important. Such a simplification often leads to key concepts that can provide guidance in tailoring the geometry and composition of surface atoms for desired properties. One of the most widely used descriptor is the d-band center ε_d , i.e., the average energy of electronic d states projected onto a surface metal atom, is such a descriptor within the theoretical framework of the d-band model of surface chemisorption. Typically, the closer in energy the center of the *d*-band is with respect to the Fermi level, more reactive the system is. The ε_d values show the following trend for icosahedral systems: $Pd_{55} < Pd_{13}@Ni_{42} < Ni_{55} < Pd_1@Ni_{54} = Au_1@Ni_{54} < Au_{55} < Au_{13}@Ni_{42}$ (Fig. 10b, d, f, h, j, l and n on the left). For the decahedral NPs the order is Pd₅₄ <- $Pd_7@Ni_{47} < Au_{54} < Ni_{54} < Au_7@Ni_{47}$ (Fig. 10b, d, f, h and j on the right). It can be noted that there is not a linear relationship between the composition of the bimetallic systems with the center of the d-band. The d-band center value is based on the degree of filling, average energy and width of the localized d-band of the metal surface and how they interact with the adsorbate energy levels. In particular, there are two simple mechanisms for changing the chemical properties of the NP. First, the average bond length between the metal atoms in the shell surface is different from that of the monometallic particle, resulting in changes of the strain. Second, hetero-metallic bonding interactions (called the 'ligand effect') between the surface atoms and the substrate can result in a change of the surface electronic structure, thereby modify the surface chemical properties. This indicates that the chemical reactivity cannot be analyzed only with the d-band center approach, because of the complex interplay between different parameters. Then, for a better understanding of NPs reactivity, charge transfer, work function (WF) and electronegativity must also be considered.

In these metallic systems, the information about the ability of the metal to gain or lose electrons could be provided from the WF and Fermi level (E_F) values. Upon metal-metal contact, electrons can freely exchange between the two conductors. In most



Fig. 11. Curves of d-band PDOS for 54-atoms decahedral systems (right). The blue and red lines indicate the spin up and spin down contributions, respectively. The black line corresponds to the total d-band curve. Schematic of the mono and bimetallic systems.

cases, the initial Fermi levels of the metals are not equal, so a net flow of electrons takes place from the material with the lower WF into the other until the Fermi levels are equal in both phases [56]. During this process, some of transferred charge will be distributed on the surfaces, generating an electric field, although most of it will be retained at the metal contact interface, like a surface dipole. This reveals an outer potential difference between M and Ni metals that is directly proportional to the WF value difference.

The WF and E_F obtained for the studied systems is listed in Table S1. The WF values are ordered as follows: Pd (5.09 eV) > Au (5.06 eV) > Ni (3.98 eV) for the Dh₅₄, and Au (5.07 eV) > Pd (4.88 eV) > Ni (4.17 eV) for the Ih₅₅ structures. The Fermi level follows the same trends. In addition, the electronegativity order of the metallic elements is Au > Pd > Ni.

These values are consistent with the electron density transfer from Ni to other metals when they are in contact, as can be seen in Fig. 12. In all of our bimetallic systems the core and the shell develop negative and positive net charge, respectively. Then, it is clear that the charge is transferred from the shell atoms to the core atoms, leading to a surface shell being partially positive. This fact agrees with electronegativity difference. In addition, a smaller WF value for M_m@Ni_n NPs compared with monometallic Ni NPs, could indicate a higher reactivity [57]. Replacing the core of Dh₅₄ Ni NP by Au- or Pd-atoms, increase the WF values about 0.08 or 0.09 eV. Finally, changing the central atom in Ih₅₅-Ni NP by Auor Pd-atom induces a decrease in the WF of about 0.12 or 0.16 eV, while if the complete core is replaced by Au- or Pdatoms the decrease is 0.13 and 0.24 eV, respectively. These results could indicate that the Pd₁₃@Ni₄₂ system is the most reactive, which is in good agreement with our experimental data. As previously mentioned by Logsdail et al., the interfacial charge transfer effects are then dependent on the inherent material WF [58].

The layer-by-layer net charge distribution (upper part of each subfigure) and the distribution of charge onto the individual atoms in the cross section (lower part of each subfigure) of $M_m@Ni_n$ sys-

tems (M = Au, Pd) are shown in Fig. 12. In this Figure, the charges have been normalized by the total amount of charge transferred from Ni to M of each particular system. It is clear that the charge is not equally distributed onto the atoms within the same layer, and also is different between layers. As expected, by analyzing the number of electrons carriers (e⁻) for each system, the layer by layer net charge distribution between the cross sections reveals that almost all of the charge transfer occurs at the nanoparticle metal-metal interface in all systems, i.e., the charge transfer is distributed within the metal phases, where the total charge is retained directly at the contact interface [56]. As predicted by WF values, in the case of Ih₅₅-M₁@Ni₅₄ and Dh₅₄-M₇@Ni₄₇, mostly of the transferences occurs form Ni-atoms to M-atoms, but some of the charge is transferred to the Ni vertex atoms too, as a geometrical property (Fig. 12c, f, e and h, respectively). In the case of Ih₅₅-M₁₃@Ni₄₂ systems the transference occurs form Ni-atoms to Matoms and there is no charge concentrated in the vertex.

Overall, our assessment is that the catalytic activity and selectivity of Au@Ni and Pd@Ni catalysts can be related to the coreshell-like structure and metal segregation withing the NPs. For these catalysts, the lattice parameter mismatch between the surrounded shell and the core, results in a strong strain in the crystal lattice over the atomic layers around the interface, thereby altering d-band center of the metals. The relative d-band center is closely associated to the molecule's adsorption, thus varying the product selectivity and catalytic activity. In contrast, the shell thickness for most of core-shell structures strongly influenced the catalytic activity via the tuned electronic effects. The M@Ni (M = Pd or Au) NPs is comprised of a Pd or Au core (-ve charge) and an outer Ni shell (+ve charge). Based on the electronic effects, the addition of Au or Pd reduced WF values for M@Ni NPs, which strengthened the OH adsorption onto the catalyst surface and then induced the GEOR intermediates removal. Ni nanoparticles adhering to the M@Ni surfaces can also employ as the catalytic active sites, and thus enhancing the active site density of these materials.



Fig. 12. Densities charge distributions for Au@Ni and Pd@Ni NPs.

4. Conclusion

In this work, Ni_xPd_{1-x} (x = 100, 98, 95 and 90 at.%) and Ni_xAu_{1-x} (x = 100, 95, 90 and 80 at.%) nanoparticles were investigated for glycerol electrooxidation (GEOR) in 1 M KOH. Based on our physiochemical characterization, Ni-rich bimetallic possess a core-shelllike structure, which is highly beneficial for GEOR. Among different atomic ratios, Ni₈₀Pd₂₀ and Ni₉₀Au₁₀ nanoparticles showed the highest current densities of 543 and 504 A.g-1, which are ~4.5 and 4.2 times of spherical Ni, respectively. The addition of Au or Pd (<20 at.%) resulted in the negative onset potential shift up to 100 mV for GEOR. 6 h electrolysis at various applied potential and temperature in combination with HPLC analysis revealed that Ni@Pd and Ni@Au tend to yield more C₃ products at any given potentials and temperatures than Ni alone. For instance, a remarkable glycerate selectivity of ~73.1% and 65.7% was achieved on Ni₈₀Pd₂₀ and Ni₉₀-Au₁₀ catalysts at 1.3 V and 50 °C, respectively. Notably, at highapplied potential (1.55 V) the monometallic Ni is mostly selective (93.1%) to formate via the C—C bonds cleavage. Overall, the coreshell-like catalytic systems produced higher current density with better selectivity to C_3 products. Theoretical calculations revealed that Pd@Ni NP is the most stable system compared to Au@Ni and monometallic Ni. In addition, on the Au@Ni NP the atomic radii mismatch produced an important strain between its layers. The excess energy indicated that the mixed shell systems are energetically more stable. Furthermore, the higher reactivity of Pd@Ni system compared to Au@Ni and monometallic Ni systems was explained based on WF, electronegativity, Bader charges and electronic structure results thus showing an excellent correlation between our experimental and theoretical findings.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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