

# Composition-tuned Pt-skinned PtNi bimetallic clusters as highly efficient methanol dehydrogenation catalysts

Ting-Wei Liao<sup>1,\*,#,†</sup>, Anupam Yadav<sup>1,#</sup>, Piero Ferrari<sup>1</sup>, Yubiao Niu<sup>2</sup>, Xian-Kui Wei<sup>3</sup>, Jerome Vernieres<sup>2</sup>, Kuo-Juei Hu<sup>1</sup>, Marc Heggen<sup>3</sup>, Rafal E. Dunin-Borkowski<sup>3</sup>, Richard E. Palmer<sup>2</sup>, Kari Laasonen<sup>4</sup>, Didier Grandjean<sup>1,\*</sup>, Ewald Janssens<sup>1</sup>, and Peter Lievens<sup>1,\*</sup>

<sup>1</sup> *Quantum Solid State Physics, Department of Physics and Astronomy, KU Leuven, Celestijnenlaan 200D, box 2414, BE-3001 Leuven, Belgium.*

<sup>2</sup> *College of Engineering, Swansea University, Bay Campus, Fabian Way, Swansea SA1 8EN, United Kingdom*

<sup>3</sup> *Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute Forschungszentrum Jülich GmbH, Jülich 52428, Germany*

<sup>4</sup> *Department of Chemistry and Materials Science, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland.*

**ABSTRACT:** Platinum is the most active anode and cathode catalyst in next-generation fuel cells using methanol as liquid source of hydrogen. Its catalytic activity can be significantly improved by alloying with 3d metals, although a precise tuning of its surface architecture is still required. Herein, we report the design of a highly active low temperature (below 0°C) methanol dehydrogenation anode catalyst with reduced CO poisoning, based on ultra-low amount of precisely-defined Pt<sub>x</sub>Ni<sub>1-x</sub> (x = 0 to 1) bimetallic clusters (BCs) deposited on inert flat oxides by Cluster Beam Deposition (CBD). These BCs feature clear composition-dependent atomic arrangements and electronic structures stemming from their nucleation mechanism that are responsible for a volcano-type activity trend peaking at the Pt<sub>0.7</sub>Ni<sub>0.3</sub> composition. Our calculations reveal that at this composition a cluster skin of Pt atoms with d-band centres downshifted by subsurface Ni atoms weakens the CO interaction that in turn triggers a significant increase in the methanol dehydrogenation activity.

## INTRODUCTION

Low temperature proton exchange membrane fuel cells (PEMFC) and high temperature solid oxide fuel cells (SOFC) are emerging as efficient, low cost and environment-friendly solutions to harvest energy from diverse renewable sources, such as hydrogen, hydrocarbons, water, bio-fatty acids and bio-alcohols. Among these sources methanol is a promising energy raw material that can be either directly electro-oxidized to power direct methanol fuel cells (DMFCs) or easily thermo-catalytically decomposed or reformed in situ into a mixture of hydrogen and carbon monoxide that is then fed into a H<sub>2</sub> fuel cell. Methanol-based fuel cells (MFCs) are more reliable than conventional H<sub>2</sub> fuel cells, as liquid methanol is easier to store and transport than hydrogen gas.<sup>1,2</sup> Although platinum is widely used as (electro)catalyst in the dehydrogenation of methanol (CH<sub>3</sub>OH),<sup>3-4</sup> its performance is limited by its modest stability and selectivity.<sup>5-7</sup> The three main drawbacks of platinum-based anode catalysts are their high cost as methanol bonds breaking requires large amounts of catalyst,<sup>8</sup> their low selectivity to generate hydrogen as end product, and their low stability in presence of carbon monoxide, a by-product of methanol dissociation (i.e. the CO poisoning effect).<sup>9,10</sup> These crucial challenges require remediation in order to

design future high performance fuel cell catalysts, for which fundamental understanding of the reaction kinetics at the atomic and molecular level are required. For this purpose, the reaction kinetics of model catalyst systems such as single Pt atoms,<sup>11</sup> Pt single crystals,<sup>12-14</sup> oxide-supported Pt thin films,<sup>15</sup> and Pt nanoparticles,<sup>6,7</sup> have been investigated intensively.

Pt-alloy nanoparticles as fuel cell catalyst have shown higher activity and enhanced tolerance to CO poisoning. Several alloying materials such as Sn, Ru, Mo, Nb, W, Ag, and Ni have been investigated.<sup>16-19</sup> Despite these efforts, the underlying mechanism for the alloy-induced activity and tolerance to the CO poisoning effect is still under debate. Some studies suggest that the co-adsorption of CO and OH groups is responsible for the induced tolerance,<sup>9</sup> while others attribute the reduced CO poisoning mainly to alloying-induced alteration of the electronic structure of platinum.<sup>20-22</sup> Density functional theory calculations (DFT)<sup>13, 23-25</sup> and experiments on few-atom clusters in the gas phase<sup>26, 27</sup> support the latter interpretation. This controversy is largely due to the lack of clear understanding of the effect of alloying on the catalyst activity. Depending on the particle size, shape, composition, spatial atomic arrangement and method of preparation, the activity can change drastically emphasizing the need for using well-characterized

materials to identify the fundamental mechanisms at work. Pt-Ni bimetallic extended surfaces<sup>28-31</sup>, nanostructures<sup>32</sup>, nanoclusters and nanoparticles<sup>8, 33, 34</sup> that have shown enhanced activity for the oxygen reduction reaction (ORR) as methanol-tolerant cathode catalyst in fuel cell applications are also considered as promising anode-related (electro)catalysts. In most cases the investigated Pt-Ni nanomaterials are produced with (electro) chemical methods that often have a limited control over the systems size and composition. Furthermore, the involvement of stabilizing chemicals in wet chemistry, such as ligand molecules, greatly alters the intrinsic properties of nanomaterials, making the understanding of their composition- and structure-dependent activity more complex.<sup>35-40</sup>

Depositing preformed Pt-based bimetallic clusters/nanoparticles, with precisely-defined size, composition and surface coverages<sup>41-44</sup> on various oxide supports, using the Cluster Beam Deposition (CBD) technology could be one of the key solutions to design better fuel-cell catalysts.<sup>45</sup> Clusters are particles typically composed of less than a thousand atoms and have dimensions smaller than a few nanometres. They have unique magnetic,<sup>46</sup> optical,<sup>47</sup> and catalytic<sup>44, 48-50</sup> properties, distinct from those of the bulk phase, which make them promising candidates for numerous applications. Their catalytic properties can be enhanced by a synergistic combination of different elements such as earth abundant Ni and precious Pt metal, which can at the same time improve significantly their activity, reduce the CO poisoning effect and the usage of abundance-critical platinum.

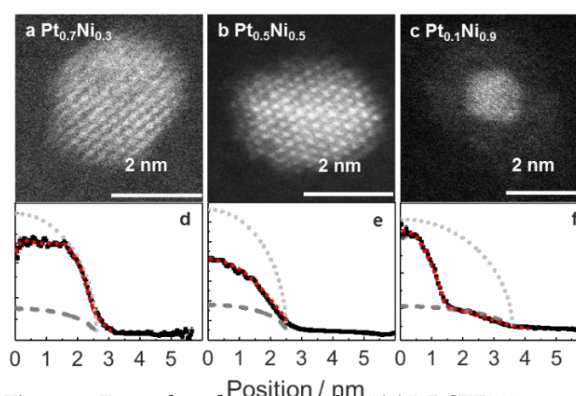
In this study, we use a laser ablation CBD source<sup>51, 52</sup> to produce and deposit Pt<sub>x</sub>Ni<sub>1-x</sub> bimetallic clusters (BCs) with an accurate control over their size and chemical composition. The BCs are deposited on two different supports, carbon TEM grids and native SiO<sub>2</sub> surfaces, with different coverages ranging from 5 % to 25 % cluster-projected area coverage (1 to 5 atomic monolayers, ML). Using a combination of high angle annular dark field scanning transmission electron microscopy (HAADF-STEM), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD), the cluster composition-dependent atomic arrangement, activity and CO poisoning in the methanol decomposition reaction are demonstrated. DFT calculations on selected sizes of the most promising Pt<sub>0.7</sub>Ni<sub>0.3</sub> composition (Pt<sub>353</sub>Ni<sub>106</sub> and Pt<sub>417</sub>Ni<sub>144</sub>) reveals that the increased catalytic activity and reduced CO poisoning effect by alloying Pt with Ni can be attributed to local d-band modifications of surface Pt-skin atoms by the presence of subsurface Ni atoms.

### COMPOSITION-TUNED SEGREGATED STRUCTURE IN Pt<sub>x</sub>Ni<sub>1-x</sub> CLUSTERS

The size distribution of Pt<sub>x</sub>Ni<sub>1-x</sub> BCs with  $x = 0.9, 0.7, 0.5, 0.3$  and  $0.1$  was characterized by STEM. The distribution of the BCs average diameters in a sample of more than 300 clusters was measured for each Pt<sub>x</sub>Ni<sub>1-x</sub> composition. A comparable size distribution (FWHMs of 1.4 nm) with an

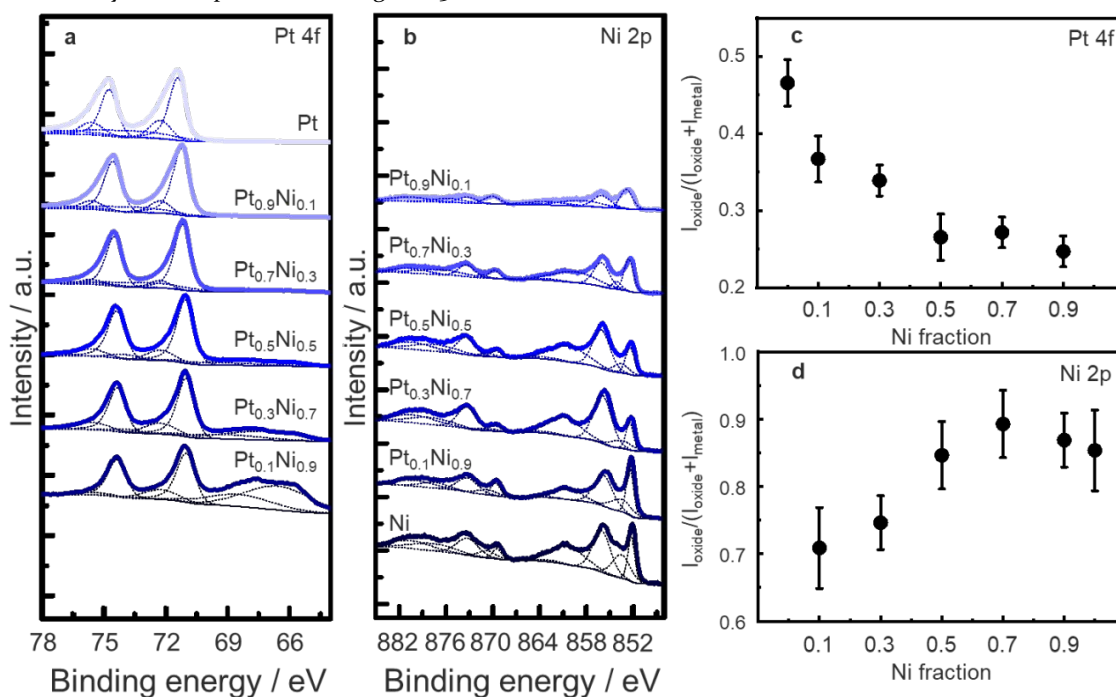
average diameter around 2.0 nm was found for all the compositions (Figure S1). In order to characterize the atomic arrangement in Pt<sub>x</sub>Ni<sub>1-x</sub> BCs, STEM images with high resolution were collected for all compositions. Given the large atomic number difference between Pt (78) and Ni (28), the atomic arrangement of these two elements within the BCs can be revealed with good contrast by their HAADF intensity profile.<sup>43, 53</sup> If phase segregation occurs, the brighter and darker parts of the BCs can be assigned to Pt-rich and Ni-rich areas, respectively. **Error! Reference source not found.** presents selected STEM images of Pt<sub>x</sub>Ni<sub>1-x</sub> BCs along with their normalised quantitative radial intensity profile integrated over the polar coordinates. Detailed inspection of the STEM images indicates that, except for the Pt<sub>0.5</sub>Ni<sub>0.5</sub> composition that is mostly alloyed, a composition-dependent phase segregation is prominent in all BCs, where the minority and majority element prefers to concentrate in the core and shell of the BCs, respectively.

This composition-tuned phase segregated atomic arrangement found in Pt-Ni BCs suggests that their formation mechanism is governed by the preferential formation of binary few-atom clusters in the nucleation stage already proposed for Au<sub>x</sub>Ag<sub>1-x</sub> BCs produced with the same source.<sup>43</sup> This is confirmed by computing and comparing the mixing energies defined as the binding energies of the small 4-atom Pt<sub>3</sub>Ni<sub>1</sub>, Pt<sub>2</sub>Ni<sub>2</sub> and Pt<sub>1</sub>Ni<sub>3</sub> BCs and their monometallic counterparts Pt<sub>4</sub> and Ni<sub>4</sub>, present in the gas-phase at the initial stages of the BCs nucleation and growth. As in the Au-Ag system, DFT calculations show that the formation of binary 4-atom clusters is energetically more favourable than that of the monometallic ones (Figure S2). This strongly suggests that these stable binary few-atom Pt-Ni clusters will form and agglomerate before the monometallic ones, to form the BCs core enriched in the minority element. The remaining pure Pt or Ni few-atom clusters of the majority elements will then condense on the Pt-Ni nuclei to form the BC shell following the same composition-tuned segregation mechanism of a general character discussed earlier.<sup>43</sup> A



**Figure 1.** Examples of atomic-scale HAADF-STEM images of Pt<sub>x</sub>Ni<sub>1-x</sub> BCs: (a, d) Pt<sub>0.7</sub>Ni<sub>0.3</sub>; (b, e) Pt<sub>0.5</sub>Ni<sub>0.5</sub>; (c, f) Pt<sub>0.1</sub>Ni<sub>0.9</sub>. The HAADF-STEM radial intensity profiles (d, e, f) are taken from the centre to the edge of the cluster and integrated from 0° to 360°. The red dotted lines correspond to simulations of cluster STEM intensity profiles with gradient composition evolution. The light grey dotted lines and dark grey dashed lines are simulated STEM intensities for pure Pt clusters and pure Ni clusters, respectively.

detailed comparison of the preparation and structure of Au-Ag and Pt-Ni systems is presented in Figure S3.



**Figure 2.** Pt 4f (a) and Ni 2p (b) XPS spectra of the  $\text{Pt}_x\text{Ni}_{1-x}$  BCs on  $\text{SiO}_2$  wafers from  $x = 0.9$  to 0.1 as well as pure Pt and Ni clusters. The Pt 4f peaks of Pt  $4f_{7/2}$  and Pt  $4f_{5/2}$  are deconvoluted into Pt metal phase (71.1 eV and 74.4 eV) and Pt oxide phases (72.3 eV, 75.7 eV, 73.9 eV and 77.3 eV); the Pt 4f XPS intensity ratio of the oxide phase is summarized in (c). The Ni 2p peaks of Ni  $2p_{3/2}$  and Ni  $2p_{1/2}$  are deconvoluted into a Ni metal phase (852.5 eV and 869.6 eV) and Ni hydroxide/oxide phases (853.2 eV, 870.7 eV, 855.9 eV, 873.4 eV, 860.4 eV, 877.9 eV); the Ni 2p XPS intensity ratio of the oxide phase is summarized in (d).

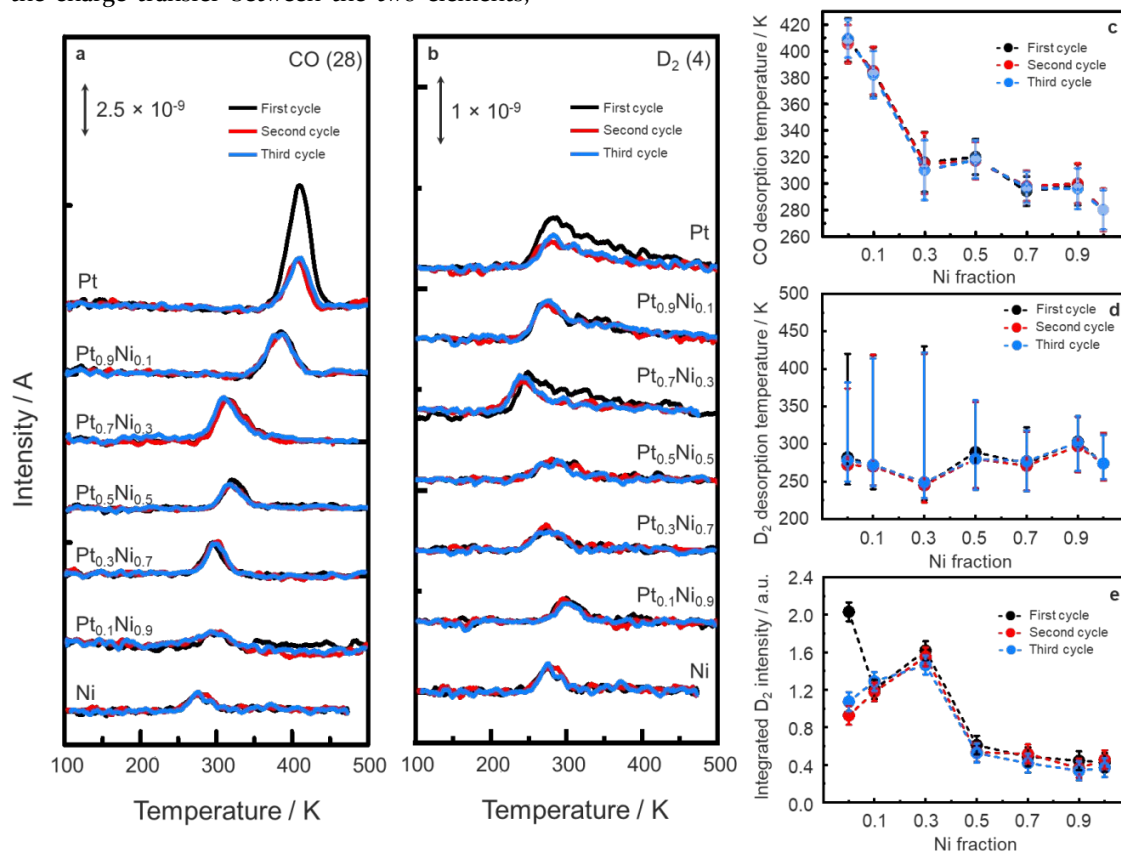
The electronic structure and the nature of the phases occurring in the air exposed  $\text{Pt}_x\text{Ni}_{1-x}/\text{SiO}_2$  ( $x = 0, 0.1, 0.3, 0.5, 0.7, 0.9$  and 1) samples were complementarily investigated by XPS. The composition and amount of the oxidized components can be revealed by deconvoluting the Pt 4f and Ni 2p peaks. The best fits of the high-resolution XPS core-level spectra in the Pt 4f and Ni 2p energy region, as well as the summary plots of Pt 4f and Ni 2p peaks with the different phases are presented in Figure 2. It is found that Pt atoms within the BCs mainly remained metallic and that a large fraction of Ni atoms was oxidized into Ni hydroxide/oxide after the samples were exposed to air. Furthermore, a composition dependent oxidation rate is observed. Pt 4f peaks can be deconvoluted into three sets of Pt  $4f_{7/2}$  and Pt  $4f_{5/2}$  peaks, corresponding to Pt metal (71.1 eV and 74.4 eV), PtO (72.3 eV and 75.7 eV) and PtO<sub>2</sub> phases (73.9 eV and 77.3 eV). Additionally, a broad peak that appears between 66 eV and 69 eV when the Ni fraction is above 0.5 can be assigned to convoluted Ni 3p peaks. The intensity evolution of these Ni 3p peaks is fully consistent with the BC composition.

Pure platinum and Pt-rich clusters feature a larger fraction of platinum oxides than their Ni-rich bimetallic counterparts. Pt oxides consist mostly of PtO with an additional contribution of the higher oxidation phase PtO<sub>2</sub> that is only present in the Pt rich BCs. In BCs with Ni fractions above 0.5, the Pt oxidation rate drops

significantly. This observation is consistent with the STEM observation that Pt atoms are predominantly present in the BC core. This suggests that their oxidation is prevented by the Ni atoms forming the BC outer shell. Similarly, the oxidation state of the Ni atoms also varies with the BC composition. The Ni  $2p_{3/2}$  and Ni  $2p_{1/2}$  peaks can be deconvoluted into Ni metal (852.5 eV and 869.6 eV), NiO (853.2 eV and 870.7 eV), Ni(OH)<sub>2</sub> (855.9 eV and 873.4 eV) and NiOOH phases (860.4 eV and 877.9 eV). The peaks centred around 863.6 eV and 880.8 eV are assigned to the satellite peaks of Ni  $2p_{3/2}$  and Ni  $2p_{1/2}$ . In Ni rich BCs, more than 70% of the Ni atoms are oxidized. Their average oxidation state tends to increase with the Ni fraction, reaching a maximum in Pt<sub>0.3</sub>Ni<sub>0.7</sub> BCs. This can be attributed to the relative stability of the Ni oxide and hydroxide phases; previous studies have shown that the electronic structure of Ni is modified by neighbouring Pt atoms, favouring Ni oxidation when these atoms are present in the BC shell.<sup>21, 22, 29</sup> When the Ni fraction decreases below 0.5, the cluster structure consists of a Ni enriched core and a Pt enriched shell, resulting in a decrease in the Ni oxidation rate. XPS analysis of the deconvoluted Pt and Ni metal peaks in  $\text{Pt}_x\text{Ni}_{1-x}$  BCs gives a clear indication of the electronic structural modification of Pt clusters upon mixing with Ni. The Pt metal 4f binding energy decreases from 71.3 eV to 71.1 eV while the Ni metal 2p binding energy increases from 852.1 eV to 852.6 eV,

compared to their respective monometallic counterparts. This binding energy change can be ascribed to a combined result of the charge transfer between the two elements,

band modification by the neighbouring element, and the different oxide fractions within the BCs after air exposure.<sup>54</sup>



**Figure 3.** TPD traces of methanol decomposition on Pt<sub>x</sub>Ni<sub>1-x</sub> BCs of different compositions on SiO<sub>2</sub> supports, showing the desorption of (a) CO and (b) D<sub>2</sub>. Overviews of the (c) CO and (d) D<sub>2</sub> desorption temperature. The desorption peaks are indicated with the full circles, while the upper and lower limit of desorption are indicated with bars. (e) The integrated amount of desorbed D<sub>2</sub> as a function of the Ni fraction in the BCs.

### CATALYTIC ACTIVITY OF Pt<sub>x</sub>Ni<sub>1-x</sub> CLUSTERS

The catalytic activity and stability of the Pt<sub>x</sub>Ni<sub>1-x</sub> ( $x = 1, 0.9, 0.7, 0.5, 0.3, 0.1, 0$ ) BCs deposited on SiO<sub>2</sub>/Si wafers and without ambient exposure, were tested under UHV by TPD in the methanol dehydrogenation reaction, by ramping the temperature from 100 K to 500 K at a rate of 4 K/s in 3 reaction cycles. The amount of hydrogen desorption is directly related to the methanol dehydrogenation catalytic activity of the BCs, whereas the CO desorption temperature is correlated to the strength of the CO poisoning effect. (see SI for more details on TPD experiment and analysis procedures)

The TPD traces for CO and D<sub>2</sub> in three subsequent cycles of methanol decomposition are shown in Figure 3, together with the dependence on the Ni content of the CO desorption temperature and the amount of D<sub>2</sub> desorption. The exclusive detection of CO and D<sub>2</sub> in the quadrupole mass spectrometer (QMS) indicates that the dominant reaction within the investigated temperature range is methanol dehydrogenation (C-D bond scission) highlighting the excellent selectivity of Pt-Ni BCs. As the same activity is measured in subsequent reaction cycles

while no CD<sub>3</sub> is formed, the C-O bond scission pathway that ultimately forms carbon deposits and poisons the catalyst surface can be safely excluded (Figure S5). From the amount of CO and D<sub>2</sub> desorption it is found that, except for monometallic Pt clusters, all BCs show a stable methanol dehydrogenation catalytic activity over the three reaction cycles. Although monometallic Pt clusters feature the highest activity of all samples in the first reaction cycle, their activity drops to a level similar to the other Pt-rich (Pt<sub>0.9</sub>Ni<sub>0.1</sub> and Pt<sub>0.7</sub>Ni<sub>0.3</sub>) BCs after the first cycle. All Pt<sub>x</sub>Ni<sub>1-x</sub> compositions have a single CO desorption feature.

The evolution of the CO desorption temperature, which is related to the strength of the CO poisoning effect shows a systematic 2-stage decrease when the Ni fraction increases (Figure 3-c). A fast decrease is observed for Ni fractions ranging from 0 to 0.3, while a slow one occurs for Ni fractions from 0.5 to 1. In BCs with a Ni fraction of 0.3, the CO poisoning effect is significantly reduced at room temperature by alloying Pt with Ni for the considered particle sizes. A low CO desorption temperature was observed in Ni rich BCs and pure Ni clusters. Since CO-Ni metal interactions are typically strong and expected to

1 result in a high CO desorption temperature of around 400  
2 K,<sup>56, 57</sup> this strongly suggests that the Ni atoms on Ni-rich  
3 cluster surfaces have interacted with traces of O<sub>2</sub> molecules  
4 inside the UHV chambers, even though the samples were  
5 transferred via a UHV transport vessel.<sup>58</sup> We therefore  
6 conclude that in the Ni rich BCs and pure Ni clusters, the  
7 CO molecules are desorbed from a Ni oxide surface.

8 The methanol dehydrogenation catalytic activity,  
9 defined by the integrated intensity of D<sub>2</sub> peaks, is stable  
10 during the three TPD cycles for all Pt<sub>x</sub>Ni<sub>1-x</sub> BCs as well as  
11 for the monometallic Ni clusters. The 50% reduction in the  
12 pure Pt clusters activity in the subsequent cycles may be  
13 assigned to the lower accessibility of the reaction sites on  
14 the cluster surface.<sup>7</sup> The variation of the D<sub>2</sub> desorption  
15 temperature versus the BC composition (Figure 3-d) shows  
16 a minimum at Pt<sub>0.7</sub>Ni<sub>0.3</sub>. D<sub>2</sub> desorbs in the 250-300 K range  
17 indicating that Ni alloyed Pt clusters are always  
18 catalytically active below room temperature. D<sub>2</sub> desorption  
19 also reveals the type of element present at the cluster  
20 surface. In Pt-rich BCs, the tail of the D<sub>2</sub> desorption feature  
21 extends even to 400 K, suggesting that D<sub>2</sub> molecules are  
22 formed and desorbed from the Pt surface,<sup>59</sup> while no  
23 desorption higher than 350 K is observed in Ni-rich BCs.  
24 This is possibly due to the presence of a Ni enriched shell  
25 at the surface.

26 A volcano-like plot relating the integrated intensity of D<sub>2</sub>  
27 desorption to the BC composition (Figure 3-e) peaking at  
28 the Pt<sub>0.7</sub>Ni<sub>0.3</sub> composition (+ 60% activity relative to pure Pt  
29 clusters) is observed. As the BCs catalytic activity reflects  
30 their surface properties, the nearly plateau observed for Ni  
31 fractions of 0.5 and up to 1 (pure Ni clusters) suggests that  
32 in these BCs the same type of atoms are present at the  
33 surface. Considering the composition-tunable phase  
34 segregated atomic arrangement observed in these BCs, a  
35 majority of Ni atoms are likely forming the surface of the  
36 Ni rich BCs. Similarly, in BCs with Ni fractions of 0.1 and  
37 0.3 the presence of a majority of Pt atoms is expected at the  
38 cluster surface. As Pt-Ni BCs tested under methanol  
39 decomposition were not exposed to air, the nature and  
40 amount of the oxide phases at the BC surface is expected  
41 to differ substantially from that of their air-exposed  
42 counterparts, determined by XPS. For Ni fractions of 0.5  
43 and up to the pure Ni, only a superficial NiO layer is likely  
44 present at the cluster surface in line with the discussion  
45 above, while for BCs with Ni fractions of 0.1 and 0.3, Pt  
46 atoms at the surface are expected to be mostly in a metallic  
47 state. The absence of CO<sub>2</sub> signal in the TPD traces of  
48 methanol decomposition (see Figure S6) further  
49 substantiates that the surface of the most active Pt<sub>0.7</sub>Ni<sub>0.3</sub>  
50 BC is free of Pt and/or Ni oxides that could have oxidized  
51 the formed CO species. Pt<sub>0.7</sub>Ni<sub>0.3</sub> BCs, which showed the  
52 best catalytic performance combined with a reduced CO  
53 poisoning, was selected for further theoretical modelling of  
54 its electronic structure.

#### 55 DFT CALCULATIONS OF PT<sub>x</sub>NI<sub>1-x</sub> CLUSTERS 56 SURFACE AND ITS CO-PT INTERACTIONS

57 In order to understand the origin of the decreased CO  
58 desorption temperature in Ni alloyed Pt clusters, the

59 electronic band structure was calculated for cluster sizes of  
60 about 2 nm and geometries in line with the observed  
structures in the STEM experiments. As Ni alloyed and  
pure Pt clusters tested for their catalytic activity in TPD  
were not exposed to air, non-oxidized Pt<sub>459</sub>, Pt<sub>561</sub>, Pt<sub>353</sub>Ni<sub>106</sub>  
and Pt<sub>417</sub>Ni<sub>144</sub> were selected as representative monometallic  
Pt clusters and Pt<sub>0.7</sub>Ni<sub>0.3</sub> BCs under methanol  
dehydrogenation conditions. The precise sizes correspond  
to closed atomic shells in FCC particles that have either the  
Wulff shape with small (100) facets (the 459 atom clusters)  
or larger (100) facets (the 561 atom clusters). Geometric  
details of the constructed clusters can be found in Figures  
4-a, 4-b and in the method section. To model the Pt<sub>353</sub>Ni<sub>106</sub>  
BC, a first isomer was constructed with random Pt-Ni alloy  
core and Pt surface, motivated by the HAADF-STEM and  
TPD results. Alternative atomic orderings that were  
considered and locally optimized are two different fully  
random alloy clusters and a Ni-core/Pt-shell cluster. The  
locally optimized random core-Pt shell structure was  
found to have the lowest energy, followed by the Ni-  
core/Pt-shell (+15.1 eV higher in total energy or 32.9 meV /  
atom). The two random configurations are energetically  
the least favourable (+16.5 eV and +16.6 eV, or 35.9  
meV/atom and 36.2 meV/atom, respectively). As the  
obtained lowest energy structure is consistent with the  
STEM experimental result in **Error! Reference source  
not found.**, further calculations were done with the  
random core-Pt shell BCs.

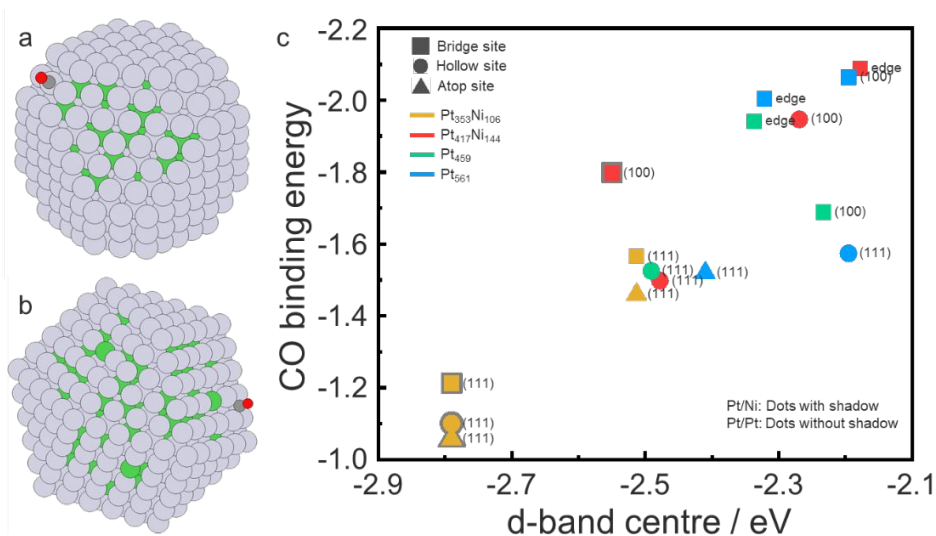
A rather simplified, however very successful, model used  
to understand the interaction of small molecules and metal  
surfaces is the d-band centre model, in which it is  
considered that on metal surfaces with a lower d-band  
centre (with respect to the Fermi level) adsorbates will  
bond less strongly.<sup>22</sup> In this model, it is considered that  
upon adsorption of a molecule on a metal surface, a  
bonding and an antibonding state are created, and the  
binding energy of the surface-molecule system will depend  
on the electron population of the adsorbate antibonding  
state that lies right above the metal d-band. The less  
populated the antibonding state is, the stronger is the  
adsorbate binding energy. This idea related the d-band  
centre of the metal surface to the adsorbate binding  
energy; surfaces with a lower d-band centre will have a  
higher electron population of the surface-molecule  
antibonding state, thus decreasing its binding energy.<sup>60</sup>

In the Pt<sub>353</sub>Ni<sub>106</sub> cluster (Figure 4-a) we distinguish two  
types of surface Pt atoms, those with another Pt atom  
subsurface and those with a subsurface Ni atom where Pt  
atoms form a skin. In the calculations of the different Pt  
atoms, the d-band centre of the first type of Pt atoms is -  
2.51 ± 0.03 eV (with respect to the Fermi level), whereas it  
is -2.79 ± 0.03 eV for the second type. The range of the d-  
band centre corresponds to the different symmetry  
inequivalent Pt sites on the surface. The d-band centre  
averaged over all Pt atoms in Pt<sub>353</sub>Ni<sub>106</sub> cluster is -2.65 eV  
compared to -2.35 ± 0.10 eV and -2.29 ± 0.12 eV in pure Pt<sub>459</sub>  
and Pt<sub>561</sub> clusters, respectively. The relative energy of the d-  
electrons is important for the CO binding and therefore,  
lowering the d-band centre of the metal should lead to a



lower CO binding strength. In order to verify this argument, we calculated binding energies of the CO molecules on various surface sites of the clusters. The correlation between the d-band centre and the CO binding

energy (see Figure 4-c), shows that the behaviour found for the CO binding energy on various Pt sites on these four clusters is consistent with the d-



**Figure 4.** (a) Wulff constructed Pt<sub>353</sub>Ni<sub>106</sub> clusters and (b) Pt<sub>417</sub>Ni<sub>144</sub> clusters constructed with larger (100) surfaces. The CO binds on both clusters on a bridge site of a (100) Pt surface. The grey, green, dark grey, and red balls represent Pt, Ni, C, and O atoms, respectively. (c) Overview of the CO binding energy as a function of the d band centre of the Pt atom on which the CO is adsorbed, for Pt atoms at the edge, (100), (111) surfaces of the Wulff constructed Pt<sub>353</sub>Ni<sub>106</sub> (orange) and larger (100) surface Pt<sub>417</sub>Ni<sub>144</sub> (red) BCs with either Pt or Ni subsurface atoms, as well as Pt<sub>459</sub> (green) and Pt<sub>561</sub> (blue) clusters. The CO adsorption on bridge site, hollow site and atop sites are presented by squares, circles and triangles, respectively. The CO adsorption on the Pt atoms with Ni subsurface atoms are indicated with grey shadow.

band model. A detailed table of all the calculated CO binding energies on different surface sites with Ni or Pt atoms at the subsurface is presented in Table S1. Although DFT calculations were performed only on two ideal clusters, we are confident that the computations captured the main trend of CO adsorption. Subsurface Ni reduces the CO binding energy on Pt, whether it is located on the flat 111 or more open 100 surfaces as well as on the edge sites. Surface defects like vacancies or adatoms are expected to alter the absolute values of the CO binding energy but very unlikely modify the general trend of a reduced CO binding energy in presence of subsurface Ni atoms. The d-electron population analysis of the BCs also reveals a substantial modification of the electronic structure of skin Pt atoms by neighbouring subsurface Ni atoms. In particular, a Löwdin population analysis<sup>61</sup> shows a reduction of their d-electron population by nearby Ni atoms, which may be in line with the model proposed by Toda et al.<sup>62</sup> The correlation between d-electron population and CO binding energy is presented in Figure S7 and Table S2. In general, independently of whether the Pt atoms are located at (100) or (111) surfaces, or at edge sites, the CO binding energy is lower if a Ni atom is present at the subsurface. Therefore, the decreased CO desorption temperature on Pt<sub>x</sub>Ni<sub>1-x</sub> BCs can be assigned to local modifications of the d-band electronic structure of surface Pt atoms forming a skin, induced by the presence of subsurface Ni, which results in a weakened CO-Pt

interaction. This is in excellent agreement with the observed reduced CO desorption temperature with Ni fraction in the methanol decomposition TPD experiments.

A maximum in the methanol activity is reached for the same Pt<sub>0.7</sub>Ni<sub>0.3</sub> cluster composition suggesting that it may be directly related to the CO poisoning of the clusters surfaces.<sup>28, 63</sup> Although our calculations show that the first methanol dissociation reaction intermediate HOCH<sub>2</sub> binds well to the Pt-skin surface of Pt<sub>353</sub>Ni<sub>106</sub> clusters, the calculated methanol binding energy on the same cluster is almost site independent and has a small value of - 0.1 eV, compared to -0.33 eV for pure Pt(111).<sup>64</sup> This is in line with previous calculations that showed that downshifting the Pt d-band centre not only results in weakening the CO binding energy but also that of the methanol itself. As the dissociative adsorption of methanol involving a first-hydrogen extraction by O-H or C-H bond scission is regarded as the rate-determining step of methanol dehydrogenation on Pt surfaces,<sup>64, 65</sup> a reduced binding energy of methanol to Pt is not expected to favour its dissociation.<sup>63</sup> This suggests that the increased methanol activity observed for the x = 0.3 composition is more related to the reduction of the CO poisoning that blocks the available Pt active sites at the surface of the cluster rather than to an increase in the intrinsic methanol dehydrogenation activity in line with the reported 60% activity increase of Pt<sub>0.7</sub>Ni<sub>0.3</sub> BCs in comparison to Pt clusters. This would be in good agreement with previous

work that identified OH and CO binding free energies as the main descriptors of the methanol dehydrogenation on metal surfaces in DMFCs.<sup>66</sup> As the reaction was carried out in UHV, the enhanced methanol activity in this work is then expected to be mainly described by the CO binding free energy. Calculated CO desorption energies ( $E_d$ ) from TPD experiments are in line with the CO binding energies computed by DFT, therefore confirming that our Pt-Ni catalysts dehydrogenate methanol selectively by forming exclusively CO and D<sub>2</sub>, excluding the formation of CD<sub>4</sub> (See SI).

This Pt-skin with subsurface Ni architecture at the surface of 2 nm Pt<sub>0.7</sub>Ni<sub>0.3</sub> BCs resembles closely those identified at the extended surfaces of Pt-Ni alloyed electrocatalysts as highly active surfaces for the ORR that occurs at the cathode of the MFC.<sup>28</sup> Interestingly, this specific Pt-skin surface architecture forms preferentially on electrodes with the similar Pt<sub>3</sub>Ni composition corresponding to the most active BCs identified in this work.<sup>28-31</sup> The computed d-band shift of ca. -2.7 eV for the Pt skin on a Pt<sub>3</sub>Ni alloy surface that corresponds to an optimal adsorption strength of the OH molecules in the ORR are in line with the corresponding value of -2.65 eV averaged over all Pt atoms and -2.8 eV for the (111) facet sites of Pt<sub>353</sub>Ni<sub>106</sub> BCs calculated in this work.<sup>28</sup> The corresponding d-band shift of -2.5 eV for the extended surfaces of pure Pt<sup>28</sup> is also in line with the values of -2.5 eV computed here for the (111) facet sites of pure Pt<sub>561</sub> and Pt<sub>459</sub>, as well as the Pt surface atoms with Pt subsurface in Pt<sub>353</sub>Ni<sub>106</sub> and Pt<sub>417</sub>Ni<sub>144</sub> clusters. This demonstrates that thermodynamically stable highly catalytic active Pt skin architectures can be created on the nanoscale surfaces of small BCs with the CBD technology. This is achieved by tuning the BC composition to Pt<sub>3</sub>Ni and taking advantage of the composition-dependent segregation profile resulting from the BCs nucleation mechanism, likely to be applicable to a variety of binary systems besides Pt-Ni.<sup>28</sup>

These results also suggest that the Pt-skin architecture that forms at the surface of Pt<sub>0.7</sub>Ni<sub>0.3</sub> clusters feature not only an enhanced catalytic activity in the methanol dehydrogenation (+60% relative to pure Pt clusters) at the anode, but also in the ORR occurring at the cathode of the MFCs. As for the ORR, the relationship between the specific methanol dehydrogenation activity and the d-band centre position on the Pt-skin surfaces exhibits a volcano-like shape. The relative methanol dehydrogenation activity of Pt<sub>0.9</sub>Ni<sub>0.1</sub> BCs (+20% relative to pure Pt clusters) suggests the formation of a Pt-surface with a Pt subsurface configuration with an estimated d-centre downshift of -2.5 eV, while for Pt<sub>0.5</sub>Ni<sub>0.5</sub>, Pt<sub>0.3</sub>Ni<sub>0.7</sub>, Pt<sub>0.1</sub>Ni<sub>0.9</sub> BCs showed a reduced activity (-50 to -60% relative to pure Pt clusters) due to the presence of an increasing amount of Ni oxide at their surfaces. As Pt-skins stable under (electro)chemical conditions<sup>28, 34</sup> can be generally obtained by a simple mild annealing of bimetallic Pt<sub>3</sub>Ni (nano)structures,<sup>28, 32</sup> we expect that the more oxidised surfaces of air-exposed Pt<sub>3</sub>Ni BCs measured by XPS can be easily transformed into a stable Pt-skin

architecture similar to that obtained in UHV after the same treatment.

CBD fabrication that enables a precise tuning of the electronic properties of bi-(multi-) metallic nanoparticles, may allow the emergence of a new generation of bi-(multi-) metallic systems with nanoscale-engineered well-defined Pt skin surfaces. These Pt-based (electro) catalysts with reduced Pt content show an enhanced catalytic activity in anode-related methanol dehydrogenation as well as in the cathode ORR, and therefore, can contribute to lowering the Pt loadings in polymer electrolyte membrane fuel cells and facilitate their utilisation as sustainable and clean energy conversion devices.

## CONCLUSIONS

The atomic arrangement and the catalytic activity of 2.0 nm gas phase Pt<sub>x</sub>Ni<sub>1-x</sub> BCs deposited on TEM grids and SiO<sub>2</sub> supports were experimentally studied by HAADF-STEM, XPS and TPD. HAADF-STEM showed that these BCs have composition-tunable atomic arrangements with minority element enriched core and majority element dominated shell structure, most likely stemming from their nucleation mechanism. The BCs oxidation and phase composition revealed by XPS confirmed their phase-segregated structure. TPD under UHV conditions show that methanol dehydrogenation via C-D and O-D bond scission occurs on the cluster surface, with CO and D<sub>2</sub> as products. A volcano-like methanol dehydrogenation catalytic activity, triggered by a strong reduction of CO poisoning effect, is obtained by alloying Pt with Ni and peaks at the Pt<sub>0.7</sub>Ni<sub>0.3</sub> composition. This is attributed by DFT calculations to a Pt-skin with subsurface Ni, where the local modifications of the Pt d-band, induced by Ni, leads to a high methanol dehydrogenation activity and weakened Pt-CO interaction, in agreement with the d-band centre model. We demonstrate a clear composition-tuned catalytic activity and CO poisoning effect of Pt-Ni BCs in the methanol decomposition reaction, explained by a composition-tuned segregation profile resulting directly from the BC nucleation mechanism. Tuning the BCs surface architecture to obtain a Pt-skin with subsurface Ni atoms, using the size and composition precision of the CBD fabrication, offers a new direction to designing long lifetime and highly active methanol fuel cell Pt-based anode but also cathode catalysts.

## METHODS/EXPERIMENTAL DETAILS

**Production of Pt<sub>x</sub>Ni<sub>1-x</sub> clusters.** Composition controlled Pt<sub>x</sub>Ni<sub>1-x</sub> ( $x = 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1$ ) BCs were produced by a combination of pulsed laser (10 Hz, Nd:YAG lasers) ablation of Pt<sub>x</sub>Ni<sub>1-x</sub> (ACI alloy, purity 99.5%) plate targets and inert gas (He, purity 99.9999%) condensation.<sup>51</sup> The size distribution of the BCs was monitored by reflectron time-of-flight (RTOF) mass spectrometry and optimized to have an average size around  $2.0 \pm 1.4$  nm. Following a supersonic expansion into vacuum, the molecular beam of Pt<sub>x</sub>Ni<sub>1-x</sub> BCs was guided to the deposition chamber and soft-landed ( $\sim 500$  m/s) on TEM grids and on SiO<sub>2</sub>/Si (100) substrates, for STEM and TPD

1 measurements, respectively.<sup>67</sup> The substrates were held at  
2 room temperature and equivalent atomic coverages of 1 ML  
3 for TEM and 5 ML for TPD were deposited. Assuming the  
4 cluster diameter is 2 nm, the projected area coverage of 1  
5 ML and 5 ML will be around 5 % and 25 %, respectively.  
6 The flux of the BCs was monitored by a quartz crystal  
7 microbalance and the BC coverage was controlled by the  
8 deposition time assuming a constant cluster flux.

9 **Structures of the Pt<sub>x</sub>Ni<sub>1-x</sub> clusters and atomic**  
10 **arrangements.** Atomic resolution STEM imaging was  
11 performed by a FEI Titan G2 80-200 Chemi-STEM  
12 operating at 200 keV and equipped with spherical  
13 aberration (Cs) probe corrector, as well as a high-angle  
14 annular dark-field (HAADF) detector. The cluster size  
15 distributions of the Pt<sub>x</sub>Ni<sub>1-x</sub> BCs were measured with low  
16 magnification in a sample of more than 300 BCs. The  
17 cluster size was determined by measuring the diameter  
18 cross-section of individual clusters. Identification of a  
19 possible core-shell structure was obtained by the Z-  
20 contrast of HAADF-STEM (Z is the elemental atomic  
21 number). The HAADF-STEM intensity is proportional to  
22 Z<sup>3.5</sup> with the camera length employed.<sup>53</sup> The large  
23 difference of the atomic number between Pt and Ni (Z<sub>Pt</sub> =  
24 78; Z<sub>Ni</sub> = 28) allows distinguishing the elemental atomic  
25 arrangement within the clusters directly from the HAADF-  
26 STEM image intensity contrast. STEM image analysis was  
27 carried out with the imageJ Fiji software. The intensity  
28 profile of each cluster was obtained by first identifying the  
29 position of the centre through averaging, and then binning  
30 the intensity in polar coordinates as a function of the radial  
31 distance to the centre.

32 **Methanol decomposition on Pt<sub>x</sub>Ni<sub>1-x</sub>/SiO<sub>2</sub>/Si (100).**  
33 Boron doped amorphous SiO<sub>2</sub>/Si(100) wafers were heated  
34 up with direct resistive heating and cleaned more than  
35 three times by a flash-heating process to 700 K to desorb  
36 all contaminations in an UHV chamber (base pressure 6 ×  
37 10<sup>-10</sup> mbar) dedicated to the TPD experiments. The  
38 desorbed contaminations were monitored by a quadruple  
39 mass spectrometer (QMS), considering the masses of H<sub>2</sub>O  
40 (18), CO/N<sub>2</sub> (28), O<sub>2</sub> (32), Ar (40), CO<sub>2</sub> (44). The sample  
41 cleaning process was terminated at the point the signal of  
42 the listed masses was reduced to the noise level. The  
43 methanol-d<sub>4</sub> (CD<sub>3</sub>OD) was purified in an UHV compatible  
44 glass test tube by repeated freeze-pump-thaw cycles to  
45 remove all the gases in the test tube and the vacuum gas  
46 lines. The methanol-d<sub>4</sub> was introduced into the UHV  
47 chamber by a leak valve and was guided to the sample  
48 surface by a dozer tube. The cleaned SiO<sub>2</sub> sample was  
49 exposed to 5 L of methanol-d<sub>4</sub> at 100 K. The methanol-d<sub>4</sub>  
50 desorption was conducted with PID controlled linear  
51 heating using a 4 K/s ramping rate and the molecule  
52 desorption was monitored by the QMS considering all  
53 possible cracking patterns. No C-H, C-O and O-H bond  
54 scission was observed on the clean SiO<sub>2</sub> surface.

55 The cleaned SiO<sub>2</sub>/Si (100) samples were then transferred  
56 in a home-built UHV transport vessel with base pressure  
57 in the 10<sup>-10</sup> mbar range to the CBD chamber with base  
58 pressure in the 10<sup>-9</sup> mbar range. After deposition of the  
59 Pt<sub>x</sub>Ni<sub>1-x</sub> BCs on the SiO<sub>2</sub>/Si (100) substrates, the samples

were transferred back to the TPD setup for methanol  
decomposition experiments. The samples were cooled  
down to 100 K by a flow of liquid nitrogen (LN<sub>2</sub>) in flexible  
stainless steel tubes and exposed to 5 L methanol-d<sub>4</sub> for  
saturation adsorption of methanol-d<sub>4</sub> on the surface. TPD  
spectra were taken in the 100 K to 500 K temperature range  
using a 4 K/s ramping rate. The catalytic experiments were  
repeated 3 times for each same sample to characterize the  
stability and catalytic activity.

**Electronic structure and oxidation state**  
**characterizations.** XPS experiments were performed at  
room temperature and under UHV conditions (base  
pressure 1.6 × 10<sup>-9</sup> mbar), but after exposure of the samples  
to air, in a Kratos Axis Supra system with a  
monochromatized Al K $\alpha$  X-ray source (1486.6 eV) operated  
at 10 mA. The spectra were collected by hemispherical  
analyser with passing energy of 160 eV and 20 eV for the  
wide scan and high-resolution spectra, respectively. The  
spectra were aligned to the adventitious carbon peak C 1s  
at 284.8 eV. The deconvolution and fitting of the peaks was  
done with CasaXPS software.<sup>68</sup> The following spin-orbit  
coupling constraints were considered: peak separations of  
17.3 eV and 3.35 eV and peak area ratios of 2/3 and 3/4 for  
Ni 2p and Pt 4f, respectively.

**DFT calculations on the electronic structures and**  
**CO / methanol - Pt interactions.** The Pt<sub>459</sub>, Pt<sub>561</sub>, Pt<sub>353</sub>Ni<sub>106</sub>  
and Pt<sub>417</sub>Ni<sub>144</sub> clusters were modelled by density functional  
theory (DFT) with the CP2K code.<sup>69-71</sup> The BLYP functional  
with GTH pseudopotentials<sup>72</sup> (18 active electrons) was used  
for both Ni and Pt. The DZVP-MOLOPT-SR basis was  
employed. The 459- and 561-atom clusters were placed in  
cubes with edge sizes of 29 Å side and 27 Å, respectively.  
Both the local atomic structure and total spin were  
optimized. The diagonalization method with the Kerker  
mixing was used in the electronic structure optimization.  
The charge decomposition analysis was performed using  
the Hirshfeld,<sup>73</sup> Bader, Löwdin, and Mulliken methods. The  
charge decomposition analysis is shown in Table S3. Two  
different type of random core-Pt shell clusters were  
constructed. The Wulff constructed Pt<sub>353</sub>Ni<sub>106</sub> cluster  
(diameter ca. 2.4 nm) was modelled with Pt surface  
tensions of 1.49 J/m<sup>2</sup> for (111) and 1.81 J/m<sup>2</sup> for (100) from Ref  
S1. (Figure 4-a). This lead to very small (100) facets of only  
four atoms. Pt<sub>417</sub>Ni<sub>144</sub> cluster (diameter ca. 2.7 nm) was  
generated with larger (100) facets (Figure 4-b). Pure Pt  
cluster has a slightly higher energy, namely 4.5 meV/atom.

## ASSOCIATED CONTENT

The **Supporting Information** is available free of charge on  
the ACS Publications website at DOI:  
10.1021/acs.chemmater.xxxxx. It contains Figures S1 to S7,  
Tables S1 to S3 and Additional material including a  
comparison of the preparation and structures of Au-Ag BCs  
with Pt-Ni BCs, the TPD experiment and analysis procedures  
and details on the DFT calculations.

## AUTHOR INFORMATION

### Corresponding Authors

\* Ting-Wei Liao: tiwei@dtu.dk



\* Didier Grandjean: didier.grandjean@kuleuven.be

\* Peter Lievens: peter.lievens@kuleuven.be

### Present Addresses

† Section for Surface Physics and Catalysis, Department of Physics, Technical University of Denmark, 2800 Kgs Lyngby, Denmark

### Author Contributions

‡ T.-W. L and A.Y. contributed equally to this manuscript. P. L., E. J., D. G., A. Y. and T.-W. L. designed the project. K.-J. H and T.-W. L. designed, constructed, and studied the reactivity in the TPD setup. A. Y., Y. N. and T.-W. L. synthesized and deposited bimetallic clusters. X.-K. W., M. H., R. E. D.-B. carried out the STEM measurements. J. V. and R. E. P. carried out the XPS measurements. P. F. and K. L. performed the DFT calculations. All authors contributed to editing and proofreading of the manuscript.

### Notes

The authors declare no competing financial interests.

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