Bimetallic Pt-Re Nanoporous Networks: Synthesis, Characterization and Catalytic Reactivity

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Abstract

The preparation of bimetallic nanoporous networks (BNNs) that combine the high surface area and thermal stability of inorganic nanostructures with the unique catalytic properties of bimetallic systems is highly desirable. Here we show a simple and highly versatile approach for synthesis of Pt-Re BNN and demonstrate the influence of preparation conditions on the BNN structure, composition and catalytic reactivity. Pt-Re BNN was prepared by reduction of double complex $[\text{Pt}(\text{NH}_3)_4][\text{Re}(\text{Cl}_6)]$ salt crystals, in which two oppositely-charged metal complexes are evenly distributed in each unit cell in a 1:1 ratio. Exposure of the salt crystals to reducing conditions induced the evaporation of the inorganic ligands, collapse of the salt structure and reduction of the metal ions for the formation of high surface area Pt-Re BNNs. Single-particle X-ray fluorescence tomography and various ensemble-based spectroscopy measurements (XPS and XANES) identified that the bulk and surface composition of the bimetallic structure and the oxidation state of the two metals can be tuned by adjusting the reduction temperature of the bimetallic salt. Pt-Re BNN showed reactivity in deoxydehydration reaction of glycerol toward the selective formation of allyl alcohol. Combination of reactivity and spectroscopic measurements revealed that enhanced reactivity was correlated to the presence of highly oxidized Re species (mostly Re^{+7}) and equal distribution of Pt and Re on the BNN surface.

Introduction

Bimetallic nanoporous networks (BNN) can merge the high catalytic selectivity of bimetallic systems¹⁻⁴ with the unique properties of nanostructures⁵⁻⁷, such as their high surface area and high density of low-coordinated surface atoms.⁸⁻¹⁰ Various approaches have been employed for synthesis of bimetallic porous materials. Among these approaches are hard- and soft-templating,¹¹⁻¹⁴ hydrothermal process¹⁵ and galvanic replacement¹⁶⁻¹⁷. However, in all these approaches there are no directing elements that ensure a controlled distribution of the two metals within the nanostructures.

A different strategy for preparation of bimetallic porous structures, which was recently introduced, is based on reduction of double complex salt crystals.¹⁸⁻²⁰ In this approach, double complex salt crystals comprising an anion complex of one metal, $[M_aL_a]^-$, and a cation complex of a second metal, $[M_bL_b]^+$ with their balancing cation and anion, marked as X^+ and Y^- , respectively, are used as precursors for the formation of BNN (eq. 1).

In these double complex salt crystals, each unit cell comprises the two metal ions in a 1:1 ratio. Salt reduction and evaporation of the inorganic ligands induce the collapse of the salt structure for the formation of high surface area BNN particles (eq. 2).¹⁸⁻²⁰

The main advantage in this approach is that the distribution of the two metals in the salt crystals is well-defined and controlled by the opposing charge of the two metal complexes. Thus, this approach ensures that the elemental ratio in the alloy is precisely predetermined. Initial studies

have demonstrated that various BNNs, such as Ag-Au, Fe-Pt and Pd-Rh, can be prepared by this synthetic approach.^{18-19, 21-22}

In this work, Pt-Re BNN was synthesized by the abovementioned double complex salt reduction approach and the influence of reduction conditions on the porosity, composition and oxidation states of the two metals were identified by various spectroscopic and microscopic techniques. In order to identify the structure-composition-reactivity correlations of Pt-Re BNN, its reactivity toward deoxydehydration (DODH) of glycerol was tested. In this reaction two adjacent hydroxyl groups are removed from vicinal diols to afford the desirable formation of allyl alcohol.²³

It was previously demonstrated that glycerol DODH reaction can be activated by either homogeneous or heterogeneous Re-based catalysts²⁴⁻²⁷ and that the reactivity can be further improved by using bimetallic systems, such as ReOx-Pd/CeO₂ and ReOx-Au/CeO₂.²⁸⁻³⁰ One of the unique advantages of Pt-Re BNN is that it is a self-supported system and therefore its catalytic properties are solely controlled by the two metals without any influence of an oxide support, which can modify the reactivity of the bimetallic catalyst.

Here we show that Pt-Re BNN is active in DODH reaction of glycerol. By tuning the preparation conditions of the BNN it was identified that improved reactivity and selectivity were correlated with higher concentration of oxidized Re species (Re⁺⁷) on the Pt-Re BNN surface.

Materials and methods

Catalyst Preparation: [Pt(NH₃)₄][Re(Cl₆)] salt crystals were prepared by mixing together an aqueous solution of [Pt(NH₃)₄]Cl₂·H₂O and an aqueous solution of K₂[Re(Cl₆)]. The mixed solution contained a 1:1 molar ratio of Pt and Re complexes. [Pt(NH₃)₄][Re(Cl₆)] salt crystals

were formed in the solution after about 5 minutes of mixing. After 2 hr, the precipitated salt crystals were collected. The salt crystals were rinsed three times with triple distilled water (TDW) to remove residues of metal complexes and then rinsed one time with acetone to remove the aqueous medium. Prior to its reduction, the salt was dried under vacuum at room temperature.

The salt crystals were reduced in a tube furnace under flow of 1 atm Ar:H₂ mixture (95% Ar and 5% H₂, 99.999%). The furnace was heated to the desired temperature (150-350 °C) at a heating rate of 15 K min⁻¹ and maintained at this temperature for 48 hr. The sample was cooled to room temperature under flow of N₂. Salt crystals were also reduced by NaBH₄. In this process the salt crystals were mixed in a water-ethanol solution with 3 equivalents of NaBH₄ for 48 hr at 0 °C. Following the reduction process the reduced particles were rinsed with TDW and then with acetone and dried under vacuum at room temperature. Monometallic Pt and Re catalysts were prepared by reduction of [Pt(NH₃)₄]Cl₂·H₂O and K₂ [Re(Cl₆)], respectively, in a tube furnace at 200 °C for 48 hr. After their reduction, all the reduced samples were kept in a desiccator.

Scanning Electron Microscopy: SEM imaging was conducted using Magellan TM 400L (FEI) microscope. The particles were supported on TEM grid or Si wafer prior to their imaging.

XPS measurements: XPS measurements were conducted using an AXIS Ultra XPS instrument (Kratos) with a focused monochromatic Al K α X-ray (1486.7 eV) source. The X-ray beam was normal to the sample and the photoelectron detector was at 45° off-normal. C1s (binding energy = 284.5 eV) was used as a reference for correction of any charging effects.

X-ray Fluorescence tomography measurements: XRF tomography measurements were performed at the P06 beamline at PETRA III synchrotron, DESY, Hamburg (Germany). A monochromatic X-ray beam of 15.0 keV was focused to a 0.5 x 0.5 μm^2 spot using KB-mirror optics (JTEC). The sample was placed in the focal spot and raster-scanned to make a point-by-

point image. The energy-dispersed fluorescent signal was detected using a 384-element Maia detector array. The Maia detector, with its large solid angle of acceptance allowed for point dwell times of 1 millisecond.³¹ Single Pt-Re particles in the size range of 40-100 μm were glued to the edge of a Kapton capillary. The capillary with the glued particle was mounted on a goniometer head and the particle was aligned to the center of rotation. For each sample from 121 to 275 projections were collected at various angles. The XRF were fitted with GeoPIXE software in order to extract element maps for every projection image.³² The resulting element maps were then aligned with imageJ software and reconstructed using an iterative Algebraic Reconstruction Technique (i-ART) algorithm with TXM-Wizard.³³ 3D datasets were visualized using the Avizo Fire software and further analysis was performed using imageJ.

X-ray Absorption Spectroscopy: Quick-XANES measurements were carried out on CLAES beamline at ALBA Synchrotron Light Source, Barcelona (Spain). The XAS data were obtained in transmission mode at the Pt LIII-edge (11.564 keV) and the Re LIII-edge (10.535 keV). The particles were mixed with carbon and pressed into pellet and then mounted in a designated in-situ cell for XAS measurements in which the sample can be exposed to elevated temperatures and varying gas environment. For the Pt LIII-edge scans, a 4 μm thick Pt foil (Goodfellow, 99.99%) was used as reference and placed between the transmission and reference ion chambers. The samples were heated at 3 $\text{K}\cdot\text{min}^{-1}$ while flowing 5% H_2 in He. A set of Quick-XANES scans was obtained while the sample was heated. Quick-XANES mode was essential in order to closely track the influence of reduction temperature on the properties of both Pt and Re in the BNN. The XAS data were processed using the Athena software for background removal, post-edge normalization, and XANES analysis. The oxidation states of the samples were determined by comparing the measured spectrum to a linear combination of the reference metal foil and the metal complexes spectra.

ICP measurements: Inductively coupled plasma-mass spectroscopy (ICP-MS) measurements were carried out (Agilent 7500cx) to determine the concentration of Re and Pt within the BNN particles. Samples were prepared by dissolving the particles in aqua regia. The solution was then diluted with TDW to obtain aqueous solution with 1 mol/mol % aqua regia.

Glycerol DODH reaction: The catalyst was loaded into a 25 mL stainless steel batch reactor (Parr Instruments) equipped with a temperature controller and a magnetically driven stirrer. The amount of catalyst loaded in the reactor was adjusted to maintain a substrate to metal mole ratio of 100:1. 5 mg (0.02 mmol) of Pt-Re black powder and 240 mg of glycerol (2.6 mmol, 100 eq.) were dissolved with 4 mL of 3-octanol in a 25 mL glass vessel. The vessel with its contents was inserted into sealed high-pressure autoclave. The reactor was purged three times with 5 atm of N₂ to ensure the removal of air from the vessel and the solution. In some cases, pretreatment of the catalyst was performed prior to addition of glycerol. In this process, the reactor was heated to 80 °C and held at this temperature for 12 hr under 10 atm of H₂. The glycerol solution was added to the reactor once the reactor temperature reached room temperature. After addition of glycerol, the reactor was purged again with 5 atm of N₂ three times. Following the reaction, fraction of the solution was extracted, diluted with ethanol and injected to a GC (Agilent) equipped with DB-1 column for products analysis.

Results and discussion

Pt-Re double complex salt crystals were synthesized by mixing a concentrated aqueous solution of the chloride salt of a cationic Pt complex, $[Pt(NH_3)_4]^{2+}$, with a solution of the potassium salt of an anionic Re complex $[ReCl_6]^{2-}$ (eq. 3).

High-Resolution Scanning Electron Microscope (HR-SEM) measurements (Fig. 1a) imaged the smooth surface structure of $[\text{Pt}(\text{NH}_3)_4][\text{Re}(\text{Cl}_6)]$ salt crystals.

Fig. 1: SEM images of Pt-Re BNN particles. Electron microscopy images demonstrate the structure of $[\text{Pt}(\text{NH}_3)_4][\text{Re}(\text{Cl}_6)]_{(s)}$ salt crystal before (a.) and after its reduction at 200 (b.) 300 (c.) and 350 °C (d.). Reduction was performed by exposure of the salt crystals to continuous flow of 1 atm H_2 :Ar mixture (5 % H_2 and 95% Ar) for 48 hours. Reduction of the salt crystals induced the formation of porous structures. Larger and more ordered ligaments were formed as the reduction temperature was increased. The insets in a and b show lower magnification SEM images of the imaged particles.

The elemental distributions of Pt and Re in a single $[\text{Pt}(\text{NH}_3)_4][\text{Re}(\text{Cl}_6)]$ crystal particle are shown in Fig. 2a and 2b, respectively. 3D imaging of the elemental distribution within single particles at ~1 micron resolution of the reconstructed volume was achieved by conducting microprobe X-ray fluorescence tomography measurements. These measurements were performed at the P06 beamline at PETRA III synchrotron, DESY (Germany).³¹ As shown in Fig. 2c, which is an

overlay of Fig. 2a and 2b, there is almost a full overlap in the spatial distribution of Pt and Re in the salt crystal.

Fig. 2: X-ray fluorescence tomography measurements of single Pt-Re particles. Virtual cross-sections through the reconstructed 3D volume with a spatial resolution of 1 μm show the distribution of Pt (marked in green, a and d), Re (marked in red, b and e) and their overlay (c and f) in Pt-Re salt crystal before (a-c) and after (d-f) its exposure to reducing conditions (200 $^{\circ}\text{C}$, 48 h, 1 atm of 5 % H_2 and 95% Ar). Scale bar is 10 μm .

The Pearson correlation coefficient value for Pt and Re in the salt particle was determined based on correlation analysis of the positions of Pt and Re in each cross section of the complete 3D crystal. Based on this analysis it was identified that the Pearson correlation coefficient value for the bimetallic salt crystals was 0.97. Thus, as expected from the well-defined salt structure, Pt and Re exhibit high spatial correlation in the salt crystal.

Exposure of the salt crystals to reducing environment (continuous flow of 5% H_2 and 95% Ar, 1 atm, 200 $^{\circ}\text{C}$, 48 h) induced the evaporation of inorganic ligands and formation of high surface area nanoporous Pt-Re BNN (eq. 4), as identified by HR-SEM measurements (Fig. 1b).

The SEM image in the inset of Fig. 1b demonstrates that the high porosity of the reduced particle did not lead to its fracturing. Larger ligaments were formed and the surface area of the BNN was reduced as the reduction temperature was increased to 300 and 350 °C (Fig. 1c and 1d, respectively).

3D imaging of a single bimetallic salt crystal identified that its exposure to reducing conditions changed its structural properties from smooth into highly corrugated (Fig. 2 d-f). Analysis of the distribution of Pt and Re within the particle (Fig. 2d and 2e, respectively) and their overlay (Fig. 2f) identified that partial segregation has occurred within the reduced particle, mainly across the particles edges in which higher density of Pt was detected. The Pearson correlation coefficient value for the reduced BNN particle was determined to be 0.85. This value is lower than the one obtained for the salt crystal (0.97) but still shows that high correlation is maintained between the positions of Pt and Re in the reduced BNN particle.

In-situ Quick X-ray Absorption Near Edge Spectroscopy (XANES) measurements were performed to identify the influence of exposure to various reducing conditions on the oxidation state of Pt and Re in Pt-Re BNN (Fig. 3). XANES measurements at the Pt LIII edge (Fig. 3a) and Re LIII edge (Fig. 3b) were conducted in a designated *in-situ* cell at the CLAEISS beamline at ALBA synchrotron³⁴ (see experimental section for details) under reducing conditions (1 atm, 5% H₂ and 95% He).

Fig. 3: XANES of Pt LIII and Re LIII edges. *In-situ* XANES measurements of the bimetallic Pt-Re salt were performed under continuous flow of 1 atm H₂:N₂ mixture (5% H₂ and 95% N₂). Pt LIII and Re LIII XANES spectra as function of the reduction temperature are shown in **a** and **b**, respectively. The percentage of metallic Pt and Re in the Pt-Re salt crystals following their exposure to various reducing conditions was calculated based on linear combination fits and is shown in **c**.

Continuous changes in the Pt XANES spectra were detected as the reduction temperature was increased until it reached 220 °C, after which no additional changes were obtained in the Pt XANES spectrum (Fig. 3a). Interestingly, an abrupt increase in the white line intensity was detected once the sample temperature reached 130 °C. This change in the XANES pattern, which occurs prior to Pt reduction, can be correlated to desorption of the inorganic ligands and the collapse of the ordered structure of the salt crystals.

At the Re XANES edge, changes were obtained until the reduction temperature reached 300 °C (Fig. 3b). Quantitative analysis of Pt and Re XANES spectra at different temperatures was

performed by fitting the measured XANES spectra to a linear combination of reference spectra (Fig. S1 and S2). The results of this analysis were summarized in Fig. 3c. It was identified that 80% of the Pt and 40% of the Re in the Pt-Re BNN were reduced into their metallic state once the bimetallic salt was reduced at 200 °C. The reduced metal percentage was increased to 90% and 60% for Pt and Re, respectively, as the reduction temperature was increased to 350 °C. Annealing of the sample to higher temperature did not noticeably change the percentage of the reduced metals. The decrease in the Re^0 percentage from 70 to 65 % as the reduction temperature was increased from 350 to 500 °C is within the error limit of the linear combination analysis.

XPS measurements of Pt 4f and Re 4f were performed to identify changes in the oxidation state and composition of Pt and Re on the surface of the BNN as function of the reduction temperature (Fig. 4a and 4b, respectively). Differently from XAS, which provides details of the electronic and structural properties of a sample over its entire volume (bulk), XPS is a surface-sensitive technique that probes the top layers of functional materials (up to 7 atomic layers in the case of Pt-Re BNN), which are often characterized by higher mobility and higher chemical activity.

Composition analysis was conducted based on XPS measurements and revealed that the Pt:Re ratio was close to 1.2:1 in the bimetallic salt (Fig. 4c). This result indicates that similar composition is found within the top layers and the bulk of the bimetallic salt crystals. As the reduction temperature was increased to 200 and 350 °C the Pt:Re ratio was changed to 3:2 and then to 9:1, respectively. Composition analysis of the entire volume of the BNN particles (bulk) was conducted by ICP measurements and revealed a Pt:Re ratio of 1:1.2 in the sample that was annealed to 350 °C. X-ray tomography and XANES measurements did not detect any changes in the bulk composition of the BNN following its reduction at 350 °C. Thus, Pt enrichment was solely detected in the top layers of the BNN and correlated to the lower surface free energy of Pt compared to Re, which makes it thermodynamically favorable for Pt to remain at the surface

when annealed, whereas Re atoms will diffuse to the bulk.³⁵ Similarly, it was previously demonstrated that the composition of the top atomic layers in bimetallic nanostructures can be widely modified following their exposure to oxidizing and reducing conditions.³⁶⁻³⁷ The changes in the composition of the top layers (~3 nm) are eventually balanced by changes in the bulk composition. However, since the ligaments diameter in the BNN that was annealed to 350 °C is ~ 100 nm (Fig. 1) only minor changes in the bulk composition are expected.

Fig. 4: XPS measurements of Pt-Re BNN. XPS measurements of Pt4f and Re4f are shown in **a** and **b**, respectively. The XPS measurements were conducted before (i) and after exposure of the sample to reducing conditions (1 atm of 5 % H₂ and 95% Ar mixture, 48 hr) at 150 (ii), 200 (iii) and 350 °C (iv). **c.** The BNN composition was analyzed based on XPS spectra. **d.** The distribution of the various oxidation states of Pt (top) and Re (bottom) in Pt-Re BNNs before and after exposure to reducing conditions were analyzed based on Gaussian fitting of the relevant XP-spectra.

The photoemission spectra of Pt and Re were analyzed using CasaXPS fitting software (curve fitting for Re and Pt XP-spectra are shown in Supp. Info. Fig. S3 and S4, respectively). The distribution of Re and Pt oxidation states following their exposure to various reducing conditions is shown in Fig. 4d.

It was identified, based on analysis of Pt XPS spectra, that Pt was continuously reduced as the reduction temperature was increased. At 200 °C most of the Pt was reduced to its metallic state with ~25% Pt⁺² species (Fig. 4d). The distribution of Pt oxidation states in the BNN did not noticeably change as the reduction temperature was increased to 350 °C. Interestingly, vast changes were obtained in the oxidation state of Re as function of the reduction temperature. Re⁺⁶ was the dominant species on the surface of the bimetallic salt crystal. But once the salt reduction temperature was raised to 200 °C, Re⁺⁷ became the dominant species. The oxidation of Re, which occurred as the reduction temperature was increased from 150 to 200 °C, was coupled with Pt reduction. Similar coupling of oxidation-reduction reaction within bimetallic systems was previously reported in Au-Pt system.³⁸

As the reduction temperature was increased to 350 °C the oxidized Re⁺⁷ was reduced to Re⁺⁴ and Re⁺². The changes in the oxidation state of Pt and Re, as detected by XPS measurements, were nicely correlated to those obtained in the XANES measurements and reflect that Re reduction is facilitated once the reduction temperature is increased from 200 to 350 °C (Fig. 3c). Based on the results gained from the various spectroscopic measurements it can be concluded that both surface composition and the oxidation state of Pt and Re can be tuned by changing the BNN reduction temperature.

The functional properties of bimetallic structures, such as for example their catalytic reactivity, are correlated to the surface composition and oxidation state of the two metallic components. In

order to identify the ways by which the surface properties of Pt and Re influence the catalytic properties of BNN, the reactivity and selectivity of Pt-Re BNN in activation of glycerol DODH reaction were studied. It was previously demonstrated that Re-based homogenous catalysts can effectively catalyze the DODH reaction of glycerol, while using secondary alcohols both as solvents and reductants.^{25, 39} Specifically, 3-octanol was demonstrated as a highly efficient reductant that led to improved allyl alcohol yield in the DODH reaction of glycerol.^{24, 40}

Batch mode reactions were performed at 160 °C under 1 atm of N₂ with 100:1 mol:mol ratio of glycerol to Pt-Re BNN. In all DODH reactions 3-octanol was used both as a solvent and as a reductant and the various products were analyzed by GC and GC-MS measurements. Pt-Re BNN particles were prepared by reduction of the bimetallic salt crystals at 200 °C. These particles were active in DODH reaction of glycerol with 98% glycerol conversion and 47% yield in the formation of allyl-alcohol after 12 hr of reaction at 160 °C (Table 1, entry 1). The additional products (except for the DODH reaction products, which are allyl-alcohol and 1-propanol) were identified by GC-MS and included various aldol condensation products that were formed by condensation reactions between glycerol and 3-octanol. The formation of similar condensation byproducts in DODH reaction of glycerol w previously reported.^{24, 41}

Table 1: DODH reaction of glycerol with Pt-Re BNN catalyst

Entry	Reduction temp. (°C) ^a	Pretreatment ^a	Conversion (%) ^b	Yield (%) ^c	Allyl-alcohol (%)	1-propanol (%)
1.	200 ^d	–	98	47	100	0
2.	350 ^d	–	84	0.05	0	0
3.	200 ^d	+	97	21	100	0
4.	0 ^e	–	97	5.4	100	0

Reaction conditions: 2.6 mmol glycerol, 5 mg catalyst, 4 ml of 3-octanol, P = 1 atm N₂, 160 °C, reaction duration = 12 hr. ^a Prior to reaction the catalyst was exposed to reducing pretreatment (10 atm H₂, 80 °C, 12 hr). ^b Yields and conversions were determined by GC measurements. ^c Yield toward DODH products formation (allyl alcohol and 1-propanol), additional products were induced by condensation reactions between glycerol and 3-octanol. ^d Catalyst was prepared by reduction of the bimetallic salt with a flow of 5% H₂ and 95% N₂ mixture for 48 hr. ^e Catalyst was reduced by mixing the bimetallic salt with 3 eq. of NaBH₄ in water-ethanol mixture for 48 hr.

GC measurements did not identify any products that were formed by C–C bond cleavage, such as ethanol or ethylene glycol. In addition, 2-propanol, 1,2-propandiol and 1,3-propandiol, which are the dominant products in glycerol hydrogenolysis reaction, were not detected. The absence of these products indicate that the deoxygenation of two adjacent hydroxyls occur in a consecutive process in one catalytic cycle without desorption and readsorption of intermediates. The yield of allyl alcohol was deteriorated once the reaction duration was extended beyond 12 hr or the reaction temperature was raised to 200 °C, mostly due to reduction of allyl alcohol to 1-propanol and higher yield of aldol-condensation products (Table S1). ICP measurements of the reaction solution were conducted to identify any leaching of the catalyst during the reaction. It was found that 0.03 w/w % of the catalyst leached into the solution phase, thus indicating a relatively high stability of the catalyst under reaction conditions.

3D imaging of the spent Pt-Re catalyst was performed to identify the influence of reaction conditions on the structure and metal distribution of the bimetallic particles (Fig. S5). Partial segregation has occurred within the spent catalyst, mainly across the edges of particle in which higher density of Pt was detected. The Pearson correlation coefficient value for the spent BNN particle was determined to be 0.81, which is lower than the one obtained for the reduced particle.

Interestingly, once the Pt-Re BNN was prepared by reduction of the bimetallic salt at 350 °C its catalytic reactivity was decreased to 84% with negligible formation of DODH products (entry 2). This experiment shows that deteriorated catalytic reactivity is obtained following exposure of the catalyst to harsher reducing conditions which changed the oxidation state and composition of Pt and Re (Fig. 4) and decreased the surface area of the BNN (Fig. 1).

In order to decouple the changes in the oxidation state, composition and surface area, which occur simultaneously once the sample is exposed to harsher reducing conditions, the active Pt-Re BNN was exposed to a reductive pretreatment at relatively low temperature (80 °C, 10 atm H₂, 12 hr). This pretreatment solely modified the oxidation state of Re (Fig. S6) and did not change the oxidation state of Pt nor the structure of the BNN. Following this pretreatment the yield of Pt-Re BNN toward the formation of allyl alcohol was decreased by twofold (entry 3).

To further demonstrate the influence of the oxidation state of Re on the BNN reactivity, the bimetallic salt was reduced by its exposure to an inorganic reducing agent at low temperature (NaBH₄, 48 hr at 0 °C). XPS measurements did not detect the presence of highly oxidized Re⁺⁷ species on the Pt-Re BNN (Fig. S7). Low yield (5.4%) was detected once the DODH reaction of glycerol was catalyzed by Pt-Re BNN that was reduced by NaBH₄ (entry 4), demonstrating the essential role of highly oxidized Re species in the selective formation of allyl alcohol.

Low reactivity (< 6% yield) was also obtained when the Pt-Re BNN was replaced with either Pt or Re monometallic nanoporous structures, which were prepared by reduction of $[Pt(NH_3)_4]Cl_2$ or $[ReCl_6]K_2$, respectively (Table S1).

The highest reactivity toward glycerol DODH reaction was obtained with Pt-Re BNN that was prepared by bimetallic salt reduction at 200 °C. The enhanced reactivity can be correlated to the presence of highly oxidized Re^{+7} and a ~1:1 Pt:Re ratio on the BNN surface (Fig. 4). Lower concentration of highly oxidized Re species was detected following exposure of the BNN to harsher reducing conditions or to a reducing pretreatment. This change was coupled with deteriorated catalytic reactivity that was observed while testing the catalytic properties of these particles.

The catalytic measurements revealed that the presence of highly oxidized Re species in the top layers of the BNN is crucial for facilitating the DODH reaction.^{24, 41} It was previously suggested that Bronsted acid sites are associated with the enhanced catalytic rate of Re in glycerol reforming under aqueous phase conditions.⁴²⁻⁴⁴ In a similar way, it is plausible that acidic Re-OH sites on the Pt-Re BNN surface facilitated the DODH reaction by direct activation of the C-OH bonds in glycerol while Pt role was to induce the formation of atomic hydrogen on the surface.

Conclusions

In this work Pt-Re BNN particles were synthesized by reduction of $[Pt(NH_3)_4][Re(Cl_6)]$ salt crystals. XANES and XPS measurements identified that Re was reduced and its surface concentration was decreased as the reduction temperature was gradually increased from 150 to 350 °C. These processes were coupled with partial surface segregation, which was detected by X-ray tomography measurements. The influence of these structural and composition changes on the catalytic reactivity of the BNN was identified by using the DODH reaction of glycerol as a model

reaction. Pt-Re BNN that was prepared by reduction of the bimetallic salt crystals at 200 °C showed the highest reactivity toward glycerol DODH reaction. The catalytic reactivity was deteriorated once the BNN was exposed to harsher reducing conditions. It was concluded, based on combination of catalytic and spectroscopic measurements, that both the presence of Pt and Re on the BNN surface in a ~ 1:1 ratio and the presence of highly oxidized Re^{+7} species are essential for maximizing the reactivity of Pt-Re BNN. These results demonstrate the ways by which the structure, composition and reactivity of Pt-Re BNN are correlated and can be tuned by varying the reduction temperature of the bimetallic salt. The absence of support or surfactant effects makes the Pt-Re BNN a unique model system for studying structure-composition-reactivity correlations within bimetallic catalysts and identifying the elements that direct the reactivity of bimetallic nanostructures.

Supporting Information

Figures showing additional X-ray tomography, XANES and XPS spectra and their fitting are included in the supporting information. Additional catalytic measurements are included as well in the supporting information.

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X-ray tomography measurements were carried out on beamline P06 at Petra III at DESY, a member of the Helmholtz Association (HGF). X-ray absorption experiments were performed at CLAESS beamline at ALBA Synchrotron. S.D. acknowledges the Israeli Ministry of Energy and the Rudin fellowship for their financial support.

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