### Accepted Manuscript

Title: Rh Nanoparticles with  $NiO_x$  Surface Decoration for Selective Hydrogenolysis of C-O Bond over Arene Hydrogenation

Author: Jiaguang Zhang Mahmoud Ibrahim Vincent Collière Hiroyuki Asakura Tsunehiro Tanaka Kentaro Teramura Karine Philippot Ning Yan



PII:	S1381-1169(16)30014-0
DOI: Poforonco:	http://dx.doi.org/doi:10.1016/j.molcata.2016.01.014
Kelelence.	MOLCAA 9740
To appear in:	Journal of Molecular Catalysis A: Chemical
Received date:	1-10-2015
Revised date:	12-1-2016
Accepted date:	13-1-2016

Please cite this article as: Jiaguang Zhang, Mahmoud Ibrahim, Vincent Colli*graveer*e, Hiroyuki Asakura, Tsunehiro Tanaka, Kentaro Teramura, Karine Philippot, Ning Yan, Rh Nanoparticles with NiOx Surface Decoration for Selective Hydrogenolysis of C-O Bond over Arene Hydrogenation, Journal of Molecular Catalysis A: Chemical http://dx.doi.org/10.1016/j.molcata.2016.01.014

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Rh Nanoparticles with  $NiO_x$  Surface Decoration for Selective Hydrogenolysis of C–O Bond over Arene Hydrogenation

Jiaguang Zhang<sup>a#</sup>, Mahmoud Ibrahim<sup>b,c#</sup>, Vincent Collière<sup>b,c</sup>, Hiroyuki Asakura<sup>d</sup>, Tsunehiro Tanaka<sup>e,f</sup>, Kentaro Teramura<sup>f,g</sup>, Karine Philippot<sup>b,c\*</sup>, Ning Yan<sup>a\*</sup>

<sup>a</sup>Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, 117585, Singapore

<sup>b</sup>CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, BP 44099, F-31077 Toulouse cedex 4, France

<sup>c</sup>Université de Toulouse, UPS, INPT,F-31077 Toulouse cedex 4, France

<sup>d</sup>Synchrotron Radiation Research Center, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan

<sup>e</sup>Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

<sup>f</sup>Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Kyoto, 615-8520, Japan

<sup>g</sup>Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

<sup>\*</sup>Corresponding authors.

<sup>#</sup>These authors contributed equally to this work



### Highlights

- NiO<sub>x</sub> decorated Rh NPs was synthesized
- NiO<sub>x</sub> segregated the terrace sites, inhibiting the coordination of benzene ring
- NiO<sub>x</sub> did not show pronounced electronic modification to the Rh core
- Hydrogenation was inhibited without compromising the C–O bond hydrogenolysis activity

#### Abstract

Surface decoration strategy is applied to design NP catalyst for the selective hydrogenolysis of C–O bond without hydrogenating benzene ring, which is critical in lignin conversion under hydrogen treatment. The synthesized NiO<sub>x</sub>/Rh NPs are featured with Rh core whose surface is partially blocked by NiO<sub>x</sub>, which segregated the surface terrace zones into smaller segments, preventing the coordination and hydrogenation of benzene rings. Moreover, the NiO<sub>x</sub> shows no electronic modification to the Rh core, thereby the blockage effect of NiO<sub>x</sub> only inhibits the hydrogenation of benzene ring but not affect the hydrogenolysis activity of Rh core.

Keywords: Surface decoration; NiO<sub>x</sub>/Rh; Nanoparticles; Selective hydrogenolysis

#### 1 Introduction

Metal nanoparticles (NPs) are widely used as catalysts for a number of reactions, owing to their potentially higher catalytic performance both in terms of activity and selectivity.[1, 2] With the rapid progress in nanotechnology over the last two decades, NPs with well-controlled size, morphology, composition and surface could be synthesized.[3] Moreover, the use of various characterization techniques could unveil the structures of NPs to an unprecedented level, and thereby rationalize the structure-activity relationships.[4-7] By controlling the nucleation and growth kinetics, NPs can be prepared with controlled sizes by regulating the experimental parameters, such as precursor concentration, stabilizer amount, and reduction temperature.[8-15] If a shape-directing agent is used in the preparation, it can direct the growth of the NPs through certain crystal directions, resulting in NPs with well-defined morphologies.[16-18] Stabilizers containing various pendent groups can provide further electron donating or withdrawing effects.[19, 20] When a second metal is introduced to form NPs, different bimetallic structures, such as core-shell [21] and nanoalloy [22, 23] systems can be obtained depending on the reaction conditions, which can lead to synergy effects. The research advances towards well-controlled NP now offer the flexibility for fine-tuning the catalytic performance of NPs, by tailoring the electronic or geometric structure of their surface.

It is anticipated that well-defined, precisely controlled, and highly active/selective NP catalysts can help to address the key challenges in future chemical industry, namely the ever increasing demand for alternative fuels and sustainable chemicals. The transformation of cellulose,[24-31] hemicellulose, [32, 33] lignin, [34-41] lipids [42, 43] and chitin [44-47] into chemicals [48-55] holds a high potential to at least complement the current fuel and commodity chemical supply. Catalysis is the technological bottleneck for the development of biomass feedstocks into chemicals. Catalysts widely used for crude oil refinery may not be easily adaptable for biorefinery, since many of the classical catalysts were developed to activate and/or functionalize the main components of fossil fuels—the hydrocarbons. Nevertheless, the biomass feedstocks are enriched in oxygen and are generally highly-functionalized with hydroxyl, carbonyl, ester, ether and aromatic groups. The high oxygen content in raw biomass and platform compounds may induce low heating value, poor stability, non-volatility, and corrosiveness (in case of carboxylic acids).[56-58] The selective defunctionalization of these feedstock sets high requirements on the catalysts. They have to be highly reactive, so that the reaction can be conducted under mild conditions to prevent decomposition of the starting materials and/or products. High selectivity is also a crucial requirement due to the co-existence of many reactive functionalities. [53, 59] For example, lignin is a highly functionalized polymer that is enriched with aromatic rings and C–O bonds. In recent years, hydrogenolysis of C–O bonds in lignin has been widely recognized as a promising strategy to break it down into monomeric compounds and oligomers, but the competitive hydrogenation of the aromatic rings is potentially a problem. [45, 60, 61] Indeed, the undesired hydrogenation reaction leads to extra consumption of dihydrogen, and generation of saturated products that are normally of lower value. Moreover, the hydrogenation reaction jeopardizes lignin hydrogenolysis. For 2phenylethyl phenyl ether, a  $\beta$ -O-4 type of lignin model compound, the C<sub>arvl</sub>-OC<sub>aliphatic</sub> bond dissociation energy is 289 kJ/mol,[62] whereas the hydrogenated counterpart possesses a Caliphatic-OC<sub>aliphatic</sub> bond with a much higher bond dissociation energy of 351 kJ/mol.[63] As such, lignin hydrogenolysis becomes much more challenging, if not impossible, in case its aromatic rings undergo hydrogenation.[60] Significant effort has been devoted to the selective hindering of the hydrogenation of aromatic rings in lignin. For instance, adding NaOH could reduce the rate of hydrogenation without compromising C-O bond hydrogenolysis, but the employment of homogeneous, strong base imposes other issues.[64]

It is well known that at the surface of a given catalyst different active sites can be responsible of parallel/competitive reactions. This provides a strategy to develop highly selective NP catalysts via specific site blockage. Several recent reports have demonstrated that the decoration of the NP surface by the addition of another metal [18, 65-67] or a metal oxide [68-70] could dramatically affect the activity and selectivity of the NPs. For example, a study concerned the doping of the surface of PVP-stabilized Pd NPs by addition of a second metal (Bi or Te) in the presence of NaBH<sub>4</sub> as reducing agent for formic acid decomposition. It appeared that while Bi favourably covered the higher index sites and led to the inhibition of dehydration reaction, Te preferentially blocked the terrace sites and reduced the rate of dehydrogenation reaction.[71] As another example, Codecorated Pt NPs synthesized via a sequential chemical reduction by alcohol in the presence of preformed Pt seeds, achieved highly selective carbonyl group reduction in the hydrogenation of  $\alpha$ , $\beta$ unsaturated aldehydes. It was proposed that the Co decoration electronically influenced the Pt surface sites to favour the carbonyl hydrogenation. [72] An alumina coating applied to  $Pd/Al_2O_3$  by atomic layer deposition made the coated catalysts low selectivity in the hydrogenation of furfural due to the surface defects site blockage by alumina. [73] Nevertheless, the effect of site blockage has not yet been extensively investigated for improving the reaction selectivity in the transformation of biomass based feedstock—a critical challenging faced in biorefinery.

In lignin hydrogenolysis, the undesired hydrogenation of aromatics requires the adsorption of benzene rings on a NP terrace whereas this is not necessary for C–O bond hydrogenolysis. As such, we envisage a strategy where an inert metal oxide is deposited on a metal NP surface to segregate terrace zones, thereby preventing benzene ring coordination and hydrogenation. Along this line, we report here the surface decoration of Rh NPs by NiO<sub>x</sub> via an organometallic approach. The olefinic complexes  $[Rh(\eta^3-C_3H_5)_3]$  and  $[Ni(\eta^4-C_8H_{12})_2]$  (also named  $Rh(allylic)_3$  and  $Ni(COD)_2$ , respectively) were employed as the metal precursors because their decomposition under dihydrogen atmosphere easily leads to the formation of NPs and alkanes as by-products which are inert towards the metal surface. Since the contamination effects from the precursors and reducing agents are eliminated, this way of NP synthesis is suitable for the exploration of the surface structure-reactivity relationships in nanocatalysis. [74-76] As shown in scheme 1, the co-decomposition of Rh(allylic)<sub>3</sub> and Ni(COD)<sub>2</sub> was conducted in THF solution at room temperature (r.t.) under 3 bar  $H_2$  and in the presence of a polymer, polyvinylpyrrolidone (PVP) as the stabilizer. This polymer is known to not interact or only weakly with a metal surface thus allowing to study "naked" metallic surfaces. On the basis of different kinetics of decomposition between the two precursors (Rh(allylic)<sub>3</sub> is decomposed at r.t. while  $Ni(COD)_2$  needs higher temperature) in the reaction conditions applied  $Rh(allylic)_3$ decomposed first and formed Rh NPs. Then Ni(COD)<sub>2</sub> was catalytically decomposed owing to the presence of Rh and Ni deposited at the surface of preformed Rh NPs. Subsequently, Ni was oxidized by exposure under air, leading to the formation of NiO<sub>x</sub>-decorated Rh NPs. It was essential to ensure Ni in the oxidation state, since Ni in the metallic state has activity in C–O bond hydrogenolysis [77, 78], which can complicate the system. For comparison purpose, pure Rh NPs and Ni NPs were prepared following the same method, and all the three catalysts have been evaluated in the hydrogenolysis of aryl ethers.

#### 2 Experimental

#### 2.1 Materials & General methods

All operations concerning the handling and synthesis of organometallic compounds and nanoparticles were carried out in Schlenck or Fischer–Porter glasswares using vacuum argon line

techniques or in a glove-box, under argon atmosphere. Bis(1,5-cyclooctadiene)nickel(0) ([Ni(COD)<sub>2</sub>]) was purchased from Sigma-Aldrich and used without further purification. Rh trisallyl (III) complex  $[Rh(\eta^3-C_3H_5)_3]$  was synthesized from the hydrated rhodium chloride salt ( $[RhCl_3 \bullet H_2O]$ ) and allylmagnesiumchloride  $[CH_2=CHCH_2MgCl]$ , both purchased from Sigma-Aldrich following a published procedure [79]. Polyvinylpyrrolidone polymer (average M.W. 40,000; Sigma-Aldrich) used as the stabilizing agent was dried under vacuum over  $P_2O_5$  at 80 °C for 3 days prior to use. Solvents used were dried using a solvent purification system (MBraun MB SPS-800). All reagents and solvents were degassed before use according to a freeze-pump-thaw process. H<sub>2</sub> was purchased from Air liquide.

#### 2.2 Synthesis of NPs

#### 2.2.1 Synthesis of Rh NPs:

 $[Rh(\eta^{3}-C_{3}H_{5})_{3}](246 \text{ mg}, 1.09 \text{ mmol})$  was introduced into a Fisher–Porter bottle and left under vacuum for 0.5 h. A solution of THF (50 mL) containing 640 mg of PVP (M.W.: 40000; Rh/PVP=10%wt), was added into the reactor under freezing temperature (-80 °C). The Fisher–Porter bottle was pressurized with dihydrogen gas (3 bar) and then warmed to r.t. After 10 min, a homogeneous black colloidal solution was observed but the reaction was kept under pressure over 16 h until completion; After elimination of excess H<sub>2</sub> under vacuum, the volume of the solution was reduced to approximately 10 mL by solvent evaporation before its transfer into a solution of deoxygenated cold pentane (100 mL). A black precipitate formed which was filtered, washed twice with pentane and dried under vacuum giving rise to the Rh NPs embedded in PVP as a crystalline black powder.

#### 2.2.2 Synthesis of Ni NPs:

 $[Ni(COD)_2]$  (300 mg, 1.09 mmol) was introduced into a Fisher–Porter bottle and left under vacuum for 0.5 h. A solution of THF (50 mL) containing 640 mg of PVP (M.W.: 40000; Rh/PVP=10%wt), was added into the reactor under freezing temperature (-80°C). The Fisher–Porter bottle was pressurized with dihydrogen gas (3 bar) and then immerged into an oil bath pre-heated at 70°C during 16 h, leading to a homogeneous black colloidal solution. After evacuation of excess H<sub>2</sub>, the volume of the solution was reduced to approximately 10 mL by solvent evaporation before its transfer into a solution of deoxygenated and cold pentane (100 mL). A black precipitate formed which was filtered, washed twice with pentane and dried under vacuum giving rise to the Ni NPs stabilized in PVP matrix as a crystalline black powder.

#### 2.2.3 Synthesis of NiO<sub>x</sub>/Rh NPs

Both  $[Ni(COD)_2]$  (150 mg, 0.55 mmol) and  $[Rh(\eta^3-C_3H_5)_3]$  (123 mg, 0.55 mmol) were introduced into a Fisher–Porter bottle and left under vacuum for 0.5 h. A solution of THF (50 mL) containing 640 mg of PVP (M.W.: 40000), was introduced into the reactor under freezing temperature (-80°C). The Fisher–Porter bottle was pressurized with hydrogen gas (3 bar) and then heated to 70°C by immersion in an oil bath. After 10 min, a homogeneous black colloidal solution was observed but the reaction was kept under pressure at 70°C over 16 h, for completion. Following a similar purification treatment as described previously for Rh and Ni NPs, RhNi NPs were obtained as a crystalline black powder. At this stage, both Rh and Ni were in the metallic state. To get the NiO<sub>x</sub>/Rh NPs, the RhNi NPs powder was taken out of the glove box and exposed in opened air for 0.5 h, before storing in the fridge.

#### 2.3 Characterization of NPs

#### 2.3.1 ICP-MS

10 mg of the NPs powder was digested with 10 ml of aqua regia under reflux conditions for 2 h, and then the mixture was diluted with deionized water to 100.0 ml. ICP-MS was recorded on Leeman ICP-MS system. Calibration standard samples were prepared by the dilution of stock solutions containing 100 ppm of Ni or Rh, which were purchased from High-Purity Standards.

#### 2.3.2 Electron Microscopy (TEM/HRTEM)

Samples for TEM/HRTEM analyses were prepared by slow evaporation of a drop of crude colloidal solution deposited on holey carbon-covered copper grids under argon (in glove-box). Transmission Electron Microscopy at low (TEM) and high resolution (HRTEM) analyses were performed at the "Centre de microcaractérisation Raimond Castaing-UMS 3623" in Toulouse. TEM images were obtained using a MET JEOL 1011 electron microscope operating at 100 kV with a resolution point of 4.5 Å or a MET JEOL JEM 1400 operating at 120 kV. HRTEM observations were carried out with a JEOL JEM 2010 electron microscope working at 200 kV with a resolution point of 2.5 Å and equipped with X-ray analysis PGT (light elements detection, resolution 135 eV).

Statistical size distributions were built by counting more than 200 non-touching particles and nanoparticle mean diameters were determined, by analyzing the TEM images with Imagetool software. The analyses were performed by assuming that the nanoparticles are spherical. Size distributions are quoted as the mean diameter ± the standard deviation. FFT (Fast Fourier Transform) electron microscopy images treatments were performed with Digital Micrograph (Version 1.80.70) to determine the crystalline structure.

#### 2.3.3 XAS

Ni K edge X-ray absorption spectra (XAS) of the NiO<sub>x</sub>/Rh and Ni NPs and reference samples (Ni foil, and NiO) were recorded at the BL01B1 beamline at the SPring-8 (Japan Synchrotron Radiation Research Institute, Hyogo, Japan) in the transmission mode at ambient temperature. A Si (111) double crystal monochromator was used to obtain a monochromatic X-ray beam. The monochromator was calibrated at the shoulder peak of the absorption edge of an X-ray absorption near edge structure (XANES) spectrum of Cu foil. Rh K-edge XAS of the NiO<sub>\*</sub>/Rh and Rh NPs and reference samples (Rh foil, and Rh<sub>2</sub>O<sub>3</sub>) were also recorded in the same manner except for the use of a Si(311) double crystal monochromator. The monochromator was calibrated at the inflection point of the XANES spectrum of the Rh foil. In both cases, higher harmonics were removed by changing glancing angles of collimation and focusing mirrors. Data reduction was carried out with Athena and Artemis included in the Ifeffit and Demeter package. For curve-fitting analysis on extended X-ray absorption fine structure (EXAFS) spectra, each theoretical scattering path was generated with FEFF6.0L, and amplitude reduction factors were estimated by curve-fitting on the reference samples. The k<sup>2</sup>-weighted EXAFS oscillation in the range of 3.0–15 Å<sup>-1</sup> was Fourier transformed, and curvefitting analyses were performed in the appropriate range in R space as described in the following section.

#### 2.3.4 XPS

XPS measurements were performed on a VG Escalab MKII spectrometer, using a mono Al K $\alpha$  X-ray source (hv = 1486.71 eV, 5 mA, 15 kV) and calibrated by setting the C 1s peak to 285.0 eV.

#### 2.3.5 SQUID

SQUID measurements were performed on a SQUID magnetometer (MPMS Quantum Design). The temperature was varied between 2 and 300 K according to a classical zero-field-cooling/field-cooling (ZFC/FC) procedure in the presence of a very weak applied magnetic field (10 Oe). The field dependent magnetization was obtained at different temperatures in a magnetic field varying from +50 kOe to -50 kOe.

#### 2.4 Catalytic reactions

In a typical experiment, the substrate (0.1 mmol, see SI for the synthesis procedure), NPs powder (0.01 mmol based on metal), 3 mL DI water and a magnetic stirrer were charged into a high pressure

reactor (20 mL). After flushing with H<sub>2</sub> for 5 times, the reactor was charged with 10 bar H<sub>2</sub>, and put into a preheated oil bath with a stirring speed of 1000 rpm. After the reaction, the reactor was quenched to ambient temperature using cooling water, and the organic products were extracted using ethyl acetate (6mL) and analyzed by gas chromatography (GC) and GC-mass spectroscopy (GC-MS) on an Agilent 7890A gas chromatograph with flame ionization detector (FID) and an Agilent 7890A-5975 GC-MS instrument, both equipped with HP-5 capillary columns (30 m × 250  $\mu$ m). The peak area was calibrated by FID effective carbon number (ECN)[80] of the representing compound. Conversion is defined as the amount of rings in products divided by the total amount of rings found on GC-FID, multiplied by 100%; the yield is defined as the amount of rings in individual product divided by the amount of rings found in products on GC-FID.

$$Conversion(\%) = \left(1 - \frac{2 \times \frac{Area_{sub}}{ECN_{sub}}}{\sum \left(\frac{Area_i}{ECN_i}\right) + 2 \times \sum \left(\frac{Area_j}{ECN_j}\right) + 2 \times \frac{Area_{sub}}{ECN_{sub}}}{\sum \left(\frac{Area_i}{ECN_i}\right) + 2 \times \sum \left(\frac{Area_j}{ECN_j}\right) + 2 \times \frac{Area_{sub}}{ECN_{sub}}}{\sum \left(\frac{Area_i}{ECN_i}\right) + 2 \times \sum \left(\frac{Area_{sub}}{ECN_{sub}}\right) \times 100\%}$$

Where n is the number of ring(s) in molecule, e.; i is subscript for monomers, while j is subscript for dimers.

#### 3 Results an Discussion

The NiO<sub>x</sub>/Rh NPs were synthesized by co-decomposing a rhodium complex  $[Rh(\eta^3-C_3H_5)_3]$  and a nickel complex  $[Ni(\eta^4-C_8H_{12})_2]$  in THF solution under 3 bar of dihydrogen and in the presence of polyvinylpyrrolidone (PVP) as a stabilizer. Although researchers have intensively studied its potential influence on the catalytic properties of NPs, [81-83] PVP is still regarded as a steric stabilizer with relatively weak interaction with metallic surfaces.[84-86] In addition, magnetic measurements performed on cobalt NPs prepared by the organometallic approach and stabilized in PVP have shown similar behavior as for bulk cobalt, supporting that the PVP has no strong effect on their surface properties.[87] As such, it was intentionally chosen to minimize the capping agent effect at the NP surface. In the presence of 3 bar H<sub>2</sub>, the THF solution containing the two precursors and PVP turned black immediately upon heating by immersing the reaction tube in an oil bath at 70°C, indicating the formation of NPs. After 16 h, purification of the NPs was performed by precipitation of the PVP-protected NPs with cold pentane followed by washing and filtration leading to a crystalline black powder. This sample of RhNi/PVP NPs was then exposed to air for 30 min to oxidize the Ni into NiO<sub>x</sub> (denoted as NiO<sub>x</sub>/Rh NPs). Rh and Ni monometallic NPs were also prepared as references in a same manner.  $[Rh(\eta^3-C_3H_5)_3]$  was immediately decomposed under same conditions (r.t., 3 bar H<sub>2</sub>). In contrast, no significant change was observed for  $[Ni(\eta^4-C_8H_{12})_2]$  solution even after stirring under 3 bar H<sub>2</sub> for 24 h. The solution only turned dark overnight when heated at 70 °C under stirring. The metal content in each isolated powder was measured by ICP-MS (Table 1). The Rh/Ni ratio in the NiO<sub>x</sub>/Rh NP sample was close to 1:1, same as the ratio of the introduced complexes, indicating the fully decomposition of both precursors. The nitrogen content in various NPs, which reflects the amount of surface PVP, was estimated from XPS analysis (Table S1). The data suggest that the PVP

content is similar among different samples which was expected since all the products were prepared by applying a M/PVP=10%wt. Figure 1a-f show typical TEM images as well as corresponding size histograms of the as-obtained NiO<sub>x</sub>/Rh, Rh and Ni NPs. Both NiO<sub>x</sub>/Rh and Rh NPs were nearly spherical and mono-dispersed with mean diameters of  $2.2 \pm 0.4$  and  $2.3 \pm 0.4$  nm, respectively. Ni NPs were nearly triangle shaped with a larger mean diameter of  $6.5 \pm 1.1$  nm, probably due to the higher temperature used in the decomposition procedure.[88]

Co-decomposed or co-reduced bimetallic systems may lead to different metal distributions, such as nanoalloys, core-shell structures, surface decoration structures, and a mixture of separated monometallic NPs. The metal distribution in RhNi bimetallic sample was firstly studied by elemental distribution analysis using STEM-EDX technique (See Figure S1). Both Rh and Ni were found present in randomly selected NPs. Although the Rh/Ni ratio varied significantly in different particles (ranging from 1:0.57 to 2.35:1) this result is a strong indication that the NPs are not a mixture of monometallic NPs and supports their bimetallic composition. Next, from the HRTEM images of NiO<sub>x</sub>/Rh NPs (Figure 1g,h), it could be clearly observed that the NPs were in well crystalline form. Only an interplanar spacing of 0.22 nm was found, corresponding to (111) spacing of fcc Rh. Considering that [Rh(allylic)<sub>3</sub>] is much more easily decomposed than [Ni(COD)<sub>2</sub>] and that the RhNi NPs have a similar particle size  $(2.2 \pm 0.4 \text{ nm}, \text{Figure 1a}, d)$  as the size of Rh NPs  $(2.3 \pm 0.4 \text{ nm}, \text{Figure 1a}, d)$ 1b,e), it is plausible that in the synthesis of NiO<sub>x</sub>/Rh NPs, [Rh(allylic)<sub>3</sub>] undergoes fast decomposition forming Rh NPs and then the Rh cores catalyze the hydrogenation of COD into cyclooctane, inducing the decomposition of [Ni(COD)<sub>2</sub>] on the Rh cores surface. The co-decomposition procedure follows an in situ seed-mediated growth mechanism, leading to the formation of NiO<sub>x</sub>/Rh NPs where the core is pure fcc Rh and surface decorated with Ni.

Since the Ni domain was not visible by HRTEM, we did a rough estimation on the surface coverage of the Rh cores (See SI). We assumed a 2.2 nm sphere particle consisting of 281 close packed Rh atoms in the core. In this case, 348 Ni atoms are required to form a close packed monolayer to fully cover the surface of Rh NPs. Compared to Rh, equal amount of Ni was used in the synthesis of RhNi NPs, which is able to cover only 80 % of Rh NP surface by forming a monolayer. The surface Ni might segregate into small islands, dividing Rh terraces into small domains (see Scheme 1). To further validate such an assumption, XPS was employed to investigate the electronic state and surface content of the NPs. As shown in Figure 2a,b for the Ni 2p region spectra for NiO<sub>x</sub>/Rh and Ni NPs, the shift of the Ni 2p<sub>3/2</sub> peak to a higher energy of around 855 eV (compared with metallic Ni which has a binding energy of 852.7 eV) and the satellite peaks at around 862 eV were observed in both samples, indicating the oxidation of metallic Ni into Ni oxide indeed occurred upon exposure to air. Figure 2c,d show the original Rh 3d spectra for NiO<sub>x</sub>/Rh and Rh NPs, as well as the deconvolutions for Rh NPs. In addition to the peaks at 307.2 eV, assigning to the binding energy of  $3d_{5/2}$  for Rh(0), peaks at about 309 eV corresponding to Rh(III) can be seen in Rh NPs, indicating the existence of positively charged Rh. These could belong to Rh atoms located on NP surface, which are commonly bearing certain positive charges.[89] Notably, the signal/noise ratio of the Rh spectrum for NiO<sub>x</sub>/Rh NPs was much lower than that of Rh NPs, which could be ascribed to the coverage of Rh core by Ni species in NiO<sub>x</sub>/Rh NPs. By integration of the Ni 2p region and Rh 3d region spectra, a surface atoms ratio of Rh/Ni = 1/4 in NiO<sub>x</sub>/Rh NPs could be estimated, which is in good accordance with ca. 80 % coverage from our model estimation.

Then the NPs were characterized by X-ray absorption spectroscopy to study at atomic scale the electronic and geometric structure of the NPs. The Ni K-edge XANES spectra of NiO<sub>x</sub>/Rh and Ni NPs (Figure 3a) showed that Ni in these NPs was mostly in oxidized form, in excellent agreement with the XPS observation (Figure 2a,b). The white line intensity of NiO<sub>x</sub>/Rh NPs was similar to the NiO reference, indicating that the Ni in NiO<sub>x</sub>/Rh NPs was almost fully oxidized. On the other hand, a medium white line intensity was observed for Ni in pure Ni NPs, suggesting pure Ni NPs contain a mixture of metallic Ni and nickel oxide. In NiO<sub>x</sub>/Rh NPs, the Ni on the surface of RhNi NPs could not form a multi-layered shell to prevent the oxidation of Ni in "inner layers", therefore all Ni was oxidized. On the other hand, the core of monometallic Ni NPs was protected by the Ni oxide outer layer, and remained in the metallic state. The Rh K-edge spectra of NiO<sub>x</sub>/Rh and Rh NPs are compiled in Figure 3b. The absorption edge for Rh NPs is in between those of Rh foil and Rh<sub>2</sub>O<sub>3</sub>, indicating the existence of positive charged Rh, in accordance with the XPS analysis. Rh in NiO<sub>x</sub>/Rh is also partial oxidized, sharing an almost same XANES with Rh NPs. This again implies that the decoration of Rh NPs by NiO<sub>x</sub> did not substantially modify the electronic properties of Rh (Figure 3b).

Similar interpretation could be drawn according to the Fourier transformed EXAFS (Figure 3c,d). The main peak in the spectrum of Ni K-edge of NiO<sub>x</sub>/Rh NPs is at ca. 1.6 Å, corresponding well to Ni–O peak. Very limited contribution of Ni–Ni peak at 2.2 Å reveals that the surface Ni on Rh core in NiO<sub>x</sub>/Rh NPs was fully oxidized. On the other hand, very similar EXAFS spectra in the spectra of Rh K-edge for Rh and RhNi NPs are observed, with similar portions of Rh–O peak at ca. 1.5 Å and Rh–Rh peak at ca. 2.3 Å. Furthermore, the EXAFS spectrum fitting was performed (Figure S3), and the derived structure parameters are compiled in

. For the Ni K-edge, the first shell for  $NiO_x/Rh$  NPs, corresponding to Ni–O, showed a coordination number of 4.6, close to the bulk NiO standard, whereas the coordination number of the second shell dropped to only 3.7, which was much smaller as compared to bulk NiO standard, indicating the segments of NiO<sub>x</sub> on Rh core were in very small size. As compared to the bulk NiO standard, the NiO<sub>x</sub> species in NiO<sub>x</sub>/Rh NPs showed a shorter Ni–O distance (2.047 Å < 2.087 Å) and a longer Ni–(O)–Ni distance (3.020 Å > 2.952 Å). Moreover, the Debye-Waller factor ( $\sigma^2$ ) for the fitting of the second shell Ni-Ni was quite large, meaning the structure was highly disordered. These results indicate that the surface NiO<sub>x</sub> might mostly exist as NiO<sub>6</sub> segments connected weakly by Ni–O–Ni connections. On the other side, the structure parameters for Ni NPs are in good accordance with the structure we proposed before, where the Ni–Ni was origin from the metallic Ni core, and the Ni–O and Ni–(O)–Ni represented the oxidized surface. For both Rh and NiO<sub>x</sub>/Rh NPs at Rh K-edge, the data could be wellfitted with Rh–O Rh–Rh but without the  $Rh_2O_3$  characteristic Rh–Rh1 or Rh–Rh2, indicating metallic Rh cores for both samples and the oxygen atoms were only located on the surface (for Rh NPs) or the interface of NiO<sub>x</sub> and Rh core (for NiO<sub>x</sub>/Rh). Notably, the Rh–Ni was involved to get a better curve fitting for the  $NiO_x/Rh$  sample, but the contribution was very low, with a coordination number of 0.6 only.

The magnetic properties of the NiO<sub>x</sub>/Rh and Ni NPs were investigated by measuring both the field dependent magnetization (M-H) and temperature dependent magnetization (ZFC-FC). In the magnetization curve M-H measured at 2K (Figure 4a), Ni NPs exhibited ferromagnetic property, the magnetization of which increased sharply with increasing field, reaching saturation magnetization  $M_s$  of 30 emu/g at nearly 10 kOe. This is consistent with the reported Ni NPs prepared and measured under similar conditions.[90] On the other hand, NiO<sub>x</sub>/Rh NPs exhibited antiferromagnetic property,

the magnetization of which did not reach saturation even when the field went up to 50 kOe, in good agreement with the reported NiO system.[91, 92] For the ZFC-FC measurement, the samples were cooled to 2 K first, in the absence of magnetic field. Then a magnetic field of 10 Oe was induced, followed by measuring of the magnetization with increasing temperature to obtain the ZFC curves as shown in Figure 4b,c in the lower curves. Subsequently, the FC curves (Figure 4b,c, the upper curves) were obtained by cooling down the samples back to 2K when keeping the external magnetic field. The two samples showed distinguished behaviours in the ZFC-FC measurements. For Ni NPs (Figure 4b), the blocking temperature ( $T_B$ ) of about 31 K could be seen as the maximum point in ZFC curve, and a splitting temperature between ZFC and FC curves could be obtained at around 95 K, in good accordance with the reported observations on Ni NPs.[93] For NiO<sub>x</sub>/Rh NPs (Figure 4c), the low magnetization decreased with increasing temperature in both ZFC and FC curves, but no characteristic temperatures could be determined from the curves. This was believed to be due to the disordered and coordination unsaturated state of the NiO on the shell of NPs.[92]

HRTEM, XPS, XAS and SQUID analysis corroborated with each other, are a strong indication, of the following key structural features for the Rh, Ni and NiO<sub>x</sub>/Rh NPs: Rh NPs were very small in size (2.3 nm), with surface being partially oxidized; Ni NPs were considerably larger (6.5 nm), and the surface is also oxidized; NiO<sub>x</sub>/Rh NPs possess a Rh core (2.2 nm) with a similar mean size as pure Rh NPs. A layer of highly disordered NiO<sub>x</sub> was found on the Rh core, covering approximately 80% of surface sites and breaking up the terrace sites into small segments. The NiO<sub>x</sub> islands barely showed any electron interaction with the Rh core but purely as a modifier tuning surface geometric properties. Thus, the NiO<sub>x</sub>/Rh NPs were suitable for revealing the surface blockage effect in tuning the selectivity of catalyst. As it will be seen hereafter, the catalytic data also support this proposed NiO<sub>x</sub>-decorated RhNPs structure, NiO<sub>x</sub>/Rh.

Rh is well-known for its excellent benzene ring hydrogenation property.[94, 95] On the other hand, its activity in C–O bond hydrogenolysis, is typically low. In order to explore the surface site blockage effect on the selective hindering of benzene ring hydrogenation without compromising C-O bond hydrogenolysis, compounds **1a-c** were selected to react with 10 bar H<sub>2</sub> in water over Rh, NiOx and NiO<sub>x</sub>/Rh NPs (Table 3). As shown in Table 3, entry 1 and Figure S5, monometallic Rh NPs showed high activity with 1a, achieving 100% conversion at 60 °C within 1 h. However, all the benzene rings in the products were saturated as a consequence of the high activity of Rh towards hydrogenation of benzene. 33% product was fully hydrogenated without C-O bond cleavage (compound 3). Not surprisingly, Ni NPs (Table 3, entry 2) displayed a very low activity (6 % conversion) despite a high selectivity towards hydrogenolysis. Under identical reaction conditions, NiO<sub>x</sub>/Rh NPs (entry 3, Figure S6) selectively catalyzed hydrogenolysis of **1a** with a moderate activity, yielding 60% aromatic products (4 + 5) with negligible hydrogenation product (1% of 2). As mentioned in previous sections, a certain size of segment is required for the hydrogenation of benzene ring over heterogeneous catalysts. A previous report suggests that Rh NPs under 1.4 nm exhibited no activity in benzene ring hydrogenation.[96] The size of Rh and NiO<sub>x</sub>/Rh NPs (2.3 nm) is slightly larger than the critical size (1.4 nm) required for benzene ring hydrogenation, which explains the good hydrogenation activity of benzene rings over pure Rh NPs. At the same time, our strategy of using NiO<sub>x</sub> for the surface partial blockage appears to be highly successful in further reducing the terrace size of the Rh domains below its critical size, so that these NPs become inactive in benzene ring hydrogenation.

Further, the reaction was conducted at r.t. to obtain more information on kinetics (entry 4-7). Reaching a conversion of 64 %, the products over pure Rh NPs were almost fully hydrogenated after merely 2 h, revealing fast hydrogenation of benzene rings, which could not be avoided by reducing

the reaction temperature. Under the same conditions, 18% conversion was achieved over NiO<sub>x</sub>decorated Rh NPs, with only less than 1% of hydrogenated products. Because the Rh content in NiO<sub>x</sub>/Rh NPs was 50% as compared to that in monometallic Rh NPs, and that ca. 80% surface in NiO<sub>x</sub>/Rh NPs was blocked by Ni, NiO<sub>x</sub>/Rh NPs had approximately 10% of surface Rh sites as compared to same amount of Rh NPs. Therefore, although NiO<sub>x</sub>/Rh NPs produced less hydrogenolysis products than Rh NPs (18:42), the TOF for the hydrogenolysis reaction, with respect to every exposed Rh sites, was much higher (180:42). Although the effect of different sites (kinks/steps vs. terraces) in the hydrogenolysis of the C-O bond of the substrate we used for this study has not been reported, hydrogenolysis reaction is well known to be structure sensitive. For instance, several works[97-100] reported that the kink/step sites are more active for hydrogenolysis of C-C bond, while terraces favour the hydrogenation/dehydrogenation reactions. Since no electronic modification was observed, the enhanced TOF in hydrogenolysis is probably likely due to the blocking of terraces which favour the hydrogenation reaction. Prolonging the reaction time to 5 h over NiO<sub>x</sub>/Rh NPs increased the yield of hydrogenolysis products to 88%, with negligible increase in hydrogenated products. Notably, the reaction was conducted with a very long duration of 40 h, but 88 % of products remained un-hydrogenated. These results demonstrate very effective inhibition of the hydrogenation by site blockage effect over the entire reaction period. Finally, additional substrates, including 1b, bearing no methoxyl substitution (entry 8-10) and 1c with one more methoxyl substitution (entry 11-13), were tested over the three NP samples. Despite the generally higher yields with 1b and lower yields with 1c ascribed to their difference in steric hindrance, similar trends were observed: Rh NPs showed 100% conversion with all the benzene rings hydrogenated; Ni NPs showed high selectivity but very low activity; NiO<sub>x</sub>/Rh exhibited moderate conversion but always with excellent inhibition of the benzene ring hydrogenation due to NiO<sub>x</sub> blockage.

#### 4 Conclusion

The selective hydrogenolysis of C–O bond without hydrogenating the benzene ring is crucial in lignin conversion. We proposed a novel catalyst designing strategy to overcome this challenge, in which an inert metal oxide is deposited on a metal NP surface to segregate its terrace zones, thereby preventing benzene ring coordination and hydrogenation. The strategy was exemplified by preparing NiO<sub>x</sub>/Rh NPs with a Rh core and a partial coverage of the surface by NiO<sub>x</sub>. The introduction of NiO<sub>x</sub> did not exhibit pronounced electronic interaction with Rh but significantly modified its geometric properties, inhibiting benzene ring hydrogenation without compromising the hydrogenolysis activity in aryl ethers. Our work thus evidences the potential of using partial site blockage to prepare highly effective catalysts for lignin conversion under dihydrogen treatment. Furthermore, this strategy might be applicable for a number of biomass related reactions, in which high demanding in catalyst selectivity and activity under mild reaction conditions are often required.

#### Acknowledgements

We thanks the Merlion project (WBS: R-279-000-421-133) for the support of staff and student exchange among Ning Yan's group and Karine Philippot's group in the past two years. CNRS is also thanked for financial support and MESR for a PhD Grant (M.I.).

#### References

[1] D. Astruc, F. Lu, J.R. Aranzaes, Angew. Chem. Int. Ed., 44 (2005) 7852-7872.

[2] D. Astruc, Nanoparticles and Catalysis, Wiley, 2008.

[3] P. Serp, K. Philippot, G.A. Somorjai, B. Chaudret, Nanomaterials in Catalysis, Wiley, 2013.

[4] K. An, G.A. Somorjai, ChemCatChem, 4 (2012) 1512-1524.

[5] E. Gross, G.A. Somorjai, J. Catal., 328 (2015) 91-101.

[6] S. Kim, D.-W. Lee, K.-Y. Lee, J. Mol. Catal. A: Chem., 391 (2014) 48-54.

[7] W. Oberhauser, M. Bartoli, G. Petrucci, D. Bandelli, M. Frediani, L. Capozzoli, C. Cepek, S. Bhardwaj, L. Rosi, J. Mol. Catal. A: Chem., 410 (2015) 26-33.

[8] T. Teranishi, M. Miyake, Chem. Mater., 10 (1998) 594-600.

[9] G. Viau, R. Brayner, L. Poul, N. Chakroune, E. Lacaze, F. Fiévet-Vincent, F. Fiévet, Chem. Mater., 15 (2003) 486-494.

[10] Y. Wang, J. Ren, K. Deng, L. Gui, Y. Tang, Chem. Mater., 12 (2000) 1622-1627.

[11] R.M. Rioux, H. Song, J.D. Hoefelmeyer, P. Yang, G.A. Somorjai, J. Phys. Chem. B, 109 (2005) 2192-2202.

[12] Y. Zhang, M.E. Grass, S.E. Habas, F. Tao, T. Zhang, P. Yang, G.A. Somorjai, J. Phys. Chem. C, 111 (2007) 12243-12253.

[13] S.M. Humphrey, M.E. Grass, S.E. Habas, K. Niesz, G.A. Somorjai, T.D. Tilley, Nano Lett., 7 (2007) 785-790.

[14] S.H. Joo, J.Y. Park, J.R. Renzas, D.R. Butcher, W. Huang, G.A. Somorjai, Nano Lett., 10 (2010) 2709-2713.

[15] C.A. Stowell, B.A. Korgel, Nano Lett., 5 (2005) 1203-1207.

[16] Y. Xia, Y. Xiong, B. Lim, S.E. Skrabalak, Angew. Chem. Int. Ed., 48 (2009) 60-103.

[17] A.R. Tao, S. Habas, P. Yang, Small, 4 (2008) 310-325.

[18] W. Niu, Y. Gao, W. Zhang, N. Yan, X. Lu, Angew. Chem. Int. Ed., 54 (2015) 8271-8274.

[19] S. Jones, J. Qu, K. Tedsree, X.-Q. Gong, S.C.E. Tsang, Angew. Chem. Int. Ed., 51 (2012) 11275-11278.

[20] S. Siankevich, Z. Fei, R. Scopelliti, G. Laurenczy, S. Katsyuba, N. Yan, P.J. Dyson, ChemSusChem, 7 (2014) 1647-1654.

[21] N. Toshima, T. Yonezawa, New J. Chem., 22 (1998) 1179-1201.

[22] R. Ferrando, J. Jellinek, R.L. Johnston, Chem. Rev., 108 (2008) 845-910.

[23] Z. Konuspayeva, G. Berhault, P. Afanasiev, T.-S. Nguyen, A. Auyezov, M. Burkitbayev, L. Piccolo, MRS Online Proceedings Library, 1641 (2014) null-null.

[24] J. Li, L. Liu, Y. Liu, M. Li, Y. Zhu, H. Liu, Y. Kou, J. Zhang, Y. Han, D. Ma, Energy Environ. Sci., 7 (2014) 393-398.

[25] Y. Liu, C. Luo, H. Liu, Angew. Chem. Int. Ed., 51 (2012) 3249-3253.

[26] R. Sun, T. Wang, M. Zheng, W. Deng, J. Pang, A. Wang, X. Wang, T. Zhang, ACS Catal., 5 (2015) 874-883.

[27] A. Fukuoka, P.L. Dhepe, Angew. Chem. Int. Ed., 45 (2006) 5161-5163.

[28] J. Hilgert, N. Meine, R. Rinaldi, F. Schuth, Energy Environ. Sci., 6 (2013) 92-96.

[29] S. Liu, Y. Okuyama, M. Tamura, Y. Nakagawa, A. Imai, K. Tomishige, ChemSusChem, 8 (2015) 571-571.

[30] M.A. Mellmer, D. Martin Alonso, J.S. Luterbacher, J.M.R. Gallo, J.A. Dumesic, Green Chem., 16 (2014) 4659-4662.

[31] R. Rinaldi, R. Palkovits, F. Schüth, Angew. Chem. Int. Ed., 47 (2008) 8047-8050.

[32] E.I. Gürbüz, J.M.R. Gallo, D.M. Alonso, S.G. Wettstein, W.Y. Lim, J.A. Dumesic, Angew. Chem. Int. Ed., 52 (2013) 1270-1274.

[33] C. Li, M. Zheng, A. Wang, T. Zhang, Energy Environ. Sci., 5 (2012) 6383-6390.

[34] Z. Luo, Y. Wang, M. He, C. Zhao, Green Chem., (2015).

[35] P.J. Deuss, M. Scott, F. Tran, N.J. Westwood, J.G. de Vries, K. Barta, J. Am. Chem. Soc., 137 (2015) 7456-7467.

[36] V. Molinari, C. Giordano, M. Antonietti, D. Esposito, J. Am. Chem. Soc., 136 (2014) 1758-1761.

[37] R. Ma, M. Guo, X. Zhang, ChemSusChem, 7 (2014) 412-415.

[38] A.K. Deepa, P.L. Dhepe, ACS Catal., 5 (2015) 365-379.

[39] X. Ouyang, X. Huang, Y. Zhu, X. Qiu, Energy & Fuels, 29 (2015) 5835-5840.

[40] C. Liu, A.K. Wilson, J. Mol. Catal. A: Chem., 399 (2015) 33-41.

[41] G.-G. Xia, B. Chen, R. Zhang, Z.C. Zhang, J. Mol. Catal. A: Chem., 388–389 (2014) 35-40.

[42] W. Li, Y. Gao, S. Yao, D. Ma, N. Yan, Green Chem., 17 (2015) 4198-4205.

[43] C.M. Garcia, S. Teixeira, L.L. Marciniuk, U. Schuchardt, Bioresour. Technol., 99 (2008) 6608-6613.

[44] N. Yan, X. Chen, Nature, 524 (2015) 155-157.

[45] Y. Pierson, X. Chen, F.D. Bobbink, J. Zhang, N. Yan, ACS Sustainable Chem. Eng., 2 (2014) 2081-2089.

[46] F.D. Bobbink, J. Zhang, Y. Pierson, X. Chen, N. Yan, Green Chem., (2014).

[47] X. Chen, S.L. Chew, F.M. Kerton, N. Yan, Green Chem., 16 (2014) 2204-2212.

[48] M. Stöcker, Angew. Chem. Int. Ed., 47 (2008) 9200-9211.

[49] J.R. Rostrup-Nielsen, Science, 308 (2005) 1421-1422.

[50] C. Somerville, H. Youngs, C. Taylor, S.C. Davis, S.P. Long, Science, 329 (2010) 790-792.

[51] T.J. Benson, P.R. Daggolu, R.A. Hernandez, S. Liu, M.G. White, Chapter Three - Catalytic Deoxygenation Chemistry: Upgrading of Liquids Derived from Biomass Processing, in: C.G. Bruce, C.J. Friederike (Eds.) Advances in Catalysis, Academic Press, 2013, pp. 187-353.

[52] M. Besson, P. Gallezot, C. Pinel, Chem. Rev., 114 (2013) 1827-1870.

[53] A.M. Ruppert, K. Weinberg, R. Palkovits, Angew. Chem. Int. Ed., 51 (2012) 2564-2601.

[54] J. Zakzeski, P.C.A. Bruijnincx, A.L. Jongerius, B.M. Weckhuysen, Chem. Rev., 110 (2010) 3552-3599.

[55] R. Herbois, S. Noel, B. Leger, S. Tilloy, S. Menuel, A. Addad, B. Martel, A. Ponchel, E. Monflier, Green Chem., 17 (2015) 2444-2454.

[56] S. Czernik, A.V. Bridgwater, Energy & Fuels, 18 (2004) 590-598.

[57] H. Wang, J. Male, Y. Wang, ACS Catal., 3 (2013) 1047-1070.

[58] A.V. Bridgwater, Biomass Bioenergy, 38 (2012) 68-94.

[59] N. Yan, P.J. Dyson, Curr. Opin. Chem. Engi., 2 (2013) 178-183.

[60] J. Zhang, J. Teo, X. Chen, H. Asakura, T. Tanaka, K. Teramura, N. Yan, ACS Catal., 4 (2014) 1574-1583.

[61] J. Zhang, H. Asakura, J.v. Rijn, J. Yang, P. Duchesne, B. Zhang, X. Chen, P. Zhang, M. Saeys, N. Yan, Green Chem., 16 (2014) 2432-2437.

[62] J. He, C. Zhao, J.A. Lercher, J. Am. Chem. Soc., 134 (2012) 20768-20775.

[63] Y.-R. Luo, P.D. Pacey, Can. J. Chem., 71 (1993) 572-577.

[64] H. Konnerth, J. Zhang, D. Ma, M.H.G. Prechtl, N. Yan, Chem. Eng. Sci., 123 (2015) 155-163.

[65] H.-X. Liu, N. Tian, M.P. Brandon, J. Pei, Z.-C. Huangfu, C. Zhan, Z.-Y. Zhou, C. Hardacre, W.-F. Lin, S.-G. Sun, PCCP, 14 (2012) 16415-16423.

[66] H. Zhang, T. Watanabe, M. Okumura, M. Haruta, N. Toshima, J. Catal., 305 (2013) 7-18.

[67] C. Wen, Y. Cui, A. Yin, K. Fan, W.-L. Dai, ChemCatChem, 5 (2013) 138-141.

[68] J. Lu, B. Fu, M.C. Kung, G. Xiao, J.W. Elam, H.H. Kung, P.C. Stair, Science, 335 (2012) 1205-1208.

[69] B.J. O'Neill, D.H.K. Jackson, A.J. Crisci, C.A. Farberow, F. Shi, A.C. Alba-Rubio, J. Lu, P.J. Dietrich, X. Gu, C.L. Marshall, P.C. Stair, J.W. Elam, J.T. Miller, F.H. Ribeiro, P.M. Voyles, J. Greeley, M. Mavrikakis,

S.L. Scott, T.F. Kuech, J.A. Dumesic, Angew. Chem. Int. Ed., 52 (2013) 13808-13812.

[70] H. Feng, J. Lu, P. Stair, J. Elam, Catal. Lett., 141 (2011) 512-517.

[71] S. Jones, S.M. Fairclough, M. Gordon-Brown, W. Zheng, A. Kolpin, B. Pang, W.C.H. Kuo, J.M. Smith, S.C.E. Tsang, Chem. Commun., 51 (2015) 46-49.

[72] S.C. Tsang, N. Cailuo, W. Oduro, A.T.S. Kong, L. Clifton, K.M.K. Yu, B. Thiebaut, J. Cookson, P. Bishop, ACS Nano, 2 (2008) 2547-2553.

[73] H. Zhang, X.-K. Gu, C. Canlas, A.J. Kropf, P. Aich, J.P. Greeley, J.W. Elam, R.J. Meyers, J.A. Dumesic, P.C. Stair, C.L. Marshall, Angew. Chem. Int. Ed., 53 (2014) 12132-12136.

[74] P. Lara, K. Philippot, L.-M. Lacroix, S. Lachaize, N. Liakakos, K. Soulantica, B. Chaudret, Organometallic Nanoparticles, in: Advances in Organometallic Chemistry and Catalysis, John Wiley & Sons, Inc., 2013, pp. 421-436.

[75] M.A. Domínguez-Crespo, E. Ramírez-Meneses, A.M. Torres-Huerta, V. Garibay-Febles, K. Philippot, Int. J. Hydrogen Energy, 37 (2012) 4798-4811.

[76] N.J.S. Costa, M. Guerrero, V. Collière, É. Teixeira-Neto, R. Landers, K. Philippot, L.M. Rossi, ACS Catal., 4 (2014) 1735-1742.

[77] Q. Song, F. Wang, J. Cai, Y. Wang, J. Zhang, W. Yu, J. Xu, Energy Environ. Sci., 6 (2013) 994-1007.

[78] A.G. Sergeev, J.D. Webb, J.F. Hartwig, J. Am. Chem. Soc., 134 (2012) 20226-20229.

[79] W.A. Herrmann, G. Brauer, Synthetic Methods of Organometallic and Inorganic Chemistry (Hermann/Brauer): Transition Metals, Thieme Medical Publishers, 2000.

[80] J.T. Scanlon, D.E. Willis, J. Chromatogr. Sci., 23 (1985) 333-340.

[81] J.N. Kuhn, C.-K. Tsung, W. Huang, G.A. Somorjai, J. Catal., 265 (2009) 209-215.

[82] Y. Borodko, H.S. Lee, S.H. Joo, Y. Zhang, G. Somorjai, J. Phys. Chem. C, 114 (2010) 1117-1126.

[83] L.R. Baker, G. Kennedy, J. Krier, M. Van Spronsen, R. Onorato, G. Somorjai, Catal. Lett., 142 (2012) 1286-1294.

[84] N. Yan, Y. Yuan, P.J. Dyson, Dalton Trans., 42 (2013) 13294-13304.

[85] N. Yan, Y. Yuan, P.J. Dyson, Chem. Commun., 47 (2011) 2529-2531.

[86] N. Yan, J. Zhang, Y. Yuan, G.-T. Chen, P.J. Dyson, Z.-C. Li, Y. Kou, Chem. Commun., 46 (2010) 1631-1633.

[87] J. Osuna, D. de Caro, C. Amiens, B. Chaudret, E. Snoeck, M. Respaud, J.-M. Broto, A. Fert, The Journal of Physical Chemistry, 100 (1996) 14571-14574.

[88] T.O. Ely, C. Amiens, B. Chaudret, E. Snoeck, M. Verelst, M. Respaud, J.-M. Broto, Chem. Mater., 11 (1999) 526-529.

[89] S.M. Baghbanian, M. Farhang, S.M. Vahdat, M. Tajbakhsh, J. Mol. Catal. A: Chem., 407 (2015) 128-136.

[90] C. Yuanzhi, P. Dong-Liang, L. Dongxing, L. Xiaohua, Nanotechnology, 18 (2007) 505703.

[91] N. Bayal, P. Jeevanandam, J. Nanopart. Res., 15 (2013) 1-15.

[92] N. Rinaldi-Montes, P. Gorria, D. Martinez-Blanco, A.B. Fuertes, L. Fernandez Barquin, J. Rodriguez Fernandez, I. de Pedro, M.L. Fdez-Gubieda, J. Alonso, L. Olivi, G. Aquilanti, J.A. Blanco, Nanoscale, 6 (2014) 457-465.

[93] E. Ramírez-Meneses, I. Betancourt, F. Morales, V. Montiel-Palma, C.C. Villanueva-Alvarado, M.E. Hernández-Rojas, J. Nanopart. Res., 13 (2011) 365-374.

[94] K.S. Weddle, J.D. Aiken, R.G. Finke, J. Am. Chem. Soc., 120 (1998) 5653-5666.

[95] J.-L. Pellegatta, C. Blandy, V. Collière, R. Choukroun, B. Chaudret, P. Cheng, K. Philippot, J. Mol. Catal. A: Chem., 178 (2002) 55-61.

[96] W.F. Graydon, M.D. Langan, J. Catal., 69 (1981) 180-192.

[97] A.K. Rovik, S.K. Klitgaard, S. Dahl, C.H. Christensen, I. Chorkendorff, Appl. Catal., A, 358 (2009) 269-278.

[98] J.H. Sinfelt, Science, 195 (1977) 641-646.

[99] R.T. Vang, K. Honkala, S. Dahl, E.K. Vestergaard, J. Schnadt, E. Lægsgaard, B.S. Clausen, J.K. Nørskov, F. Besenbacher, Nature Materials, 4 (2005) 160-162.

[100] G. Jones, J.G. Jakobsen, S.S. Shim, J. Kleis, M.P. Andersson, J. Rossmeisl, F. Abild-Pedersen, T. Bligaard, S. Helveg, B. Hinnemann, J.R. Rostrup-Nielsen, I. Chorkendorff, J. Sehested, J.K. Nørskov, J. Catal., 259 (2008) 147-160.

**Figure Captions** 



Figure 1. TEM images of (a)  $NiO_x/Rh$ , (c) Rh, and (e) Ni NPs, and the corresponding size histograms (b), (d), and (f), respectively. (g)(h) HRTEM images of  $NiO_x/Rh$ .

#### CC P 4 0



3d region.



Figure 3. (a) Ni and (b) Rh K-edge XANES spectra of NiO<sub>x</sub>/Rh, Ni, and Rh NPs. Fourier transformed (c) Ni and (d) Rh K-edge EXAFS spectra of NiO<sub>x</sub>/Rh, Ni and Rh NPs. The spectra of Ni foil, Rh foil, NiO, and Rh<sub>2</sub>O<sub>3</sub> are included as references.



Figure 4. (a) Magnetization curve M–H of NiO<sub>x</sub>/Rh and Ni NPs measured at 2 K (Inset: enlargement of low field). ZFC-FC curves for (b) Ni and (c) NiO<sub>x</sub>/Rh NPs.



Scheme 1. Schematic procedure of the one pot seed-mediated synthesis of  $NiO_x/Rh$  NPs.

#### Tables

Table 1. Composition of purified NPs powders determined by ICP-OES.

Entry	Sample	Rh (wt%)	Ni (wt%)	Rh/Ni (mol/mol)
1	NiO <sub>x</sub> /Rh	7.71	4.40	0.99:1.00
2	Rh	14.50	n.d.	1:0
3	Ni	n.d.	9.11	0:1
-				

			$CN^{b}$	<i>R</i> (Å)	<i>∆E</i> (eV)	$\sigma^2$ (Å <sup>2</sup> )
Ni-K	NiO <sub>x</sub> /Rh NPs <sup>d</sup>	Ni-O	$5.0 \pm 0.3$	2.047 ± 0.005	$1.4 \pm 0.9$	0.0064 ± 0.0006
		Ni-(O)-Ni	3.7 ± 2.1	$3.020 \pm 0.044$	$3.0 \pm 5.1$	0.0191 ± 0.0059
	Ni NPs <sup>d</sup>	Ni-O	$3.4 \pm 0.6$	2.046 ± 0.015	$0.1 \pm 1.8$	0.0090 ± 0.0022
		Ni-Ni	$3.4 \pm 0.6$	$2.468 \pm 0.010$	-3.3 ± 2.3	0.0068 ± 0.0010
		Ni-(O)-Ni	6.8 ± 1.2	2.957 ± 0.014	$0.1 \pm 1.8$	0.0127 ± 0.0015
	Ni foil <sup>d</sup>	Ni-Ni	12 <sup>c</sup>	2.483 ± 0.002	-0.7 ± 0.0	0.0061 ± 0.0002
	NiO <sup>d</sup>	Ni-O	6 <sup>c</sup>	2.087 ± 0.002	$1.5 \pm 0.8$	0.0061 ± 0.0009
		Ni-(O)-Ni	12 <sup>c</sup>	2.952 ± 0.002	-	0.0062 ± 0.0004
Rh-K	NiO <sub>x</sub> /Rh NPs <sup>e</sup>	Rh-O	$2.4 \pm 0.4$	$2.021 \pm 0.011$	-3.1 ± 2.8	0.0047 ± 0.0011
		Rh-Ni	$0.6 \pm 0.3$	2.576 ± 0.026	0.5 ± 5.2	0.0034 ± 0.0019
		Rh-Rh	4.8 ± 0.9	$2.655 \pm 0.011$	-5.0 ± 1.5	$0.0080 \pm 0.0011$
	Rh NPs <sup>e</sup>	Rh-O	2.5 ± 0.6	2.019 ± 0.015	-2.1 ± 3.6	0.0048 ± 0.0016
		Rh-Rh	5.7 ± 0.6	2.677 ± 0.005	-5.0 ± 1.2	0.0075 ± 0.0006
	Rh foil <sup>e</sup>	Rh-Rh	12 <sup>c</sup>	$2.688 \pm 0.002$	-4.1 ± 0.5	0.0042 ± 0.0002
	Rh <sub>2</sub> O <sub>3</sub> <sup>e</sup>	Rh-O	6 <sup>c</sup>	2.043 ± 0.015	$1.0 \pm 1.6$	0.0030 ± 0.0007
		Rh-Rh1	1 <sup>c</sup>	2.735 ± 0.020	-	0.0027 ± 0.0009
		Rh-Rh2	3 <sup>c</sup>	$3.010 \pm 0.022$	-	0.0033 ± 0.0005

Table 2. Structure parameters by curve fitting of FT-EXAFS.<sup>a</sup>

<sup>a</sup>Amplitude reduction factor of Ni and Rh were estimated from Ni foil, NiO, Rh foil and Rh<sub>2</sub>O<sub>3</sub> reference samples. <sup>b</sup>CN, coordination number. <sup>c</sup>Fixed when fitting. Curve-fitting analyses were performed in the range 1.2–3.0<sup>d</sup> or 1.1–3.0<sup>e</sup> Å in R space.

Table 3. Hydrogenolysis of 1-benzoxy-2-methoxy-benzene using NiO<sub>x</sub>/Rh, Rh, and Ni NPs as catalysts.<sup>a</sup>



Entry	Substrate	Catalyst	Temp (°C)	Time (h)	Conv. (%)	Yield (%)			
						2	3	4 + 5	6 + 7
1	1a	Rh	60	1	100	0	33	0	67
2	1a	Ni	60	1	6	0	0	6	0
3	1a	NiO <sub>x</sub> /Rh	60	1	61	1	0	60	0
4	1a	Rh	25	2	64	1	21	0	42
5	1a	NiO <sub>x</sub> /Rh	25	2	18	0	0	17	1
6	1a	NiO <sub>x</sub> /Rh	25	5	91	1	0	88	2
7	1a	NiO <sub>x</sub> /Rh	25	40	100	0	0	88	12
8	1b	Rh	60	1	100	0	31	0	69
9	1b	Ni	60	1	10	0	0	10	0
10	1b	NiO <sub>x</sub> /Rh	60	1	66	0	0	65	1
11	1c	Rh	60	1	100	0	48	0	52
12	1c	Ni	60	1	3	0	0	3	0
13	1c	NiO <sub>x</sub> /Rh	60	1	50	0	0	50	0

<sup>a</sup>Reaction conditions: 0.1 mmol substrate, 10 mol% NPs, 3 ml  $H_2O$ , 10 bar  $H_2$ .