

Bimetallic Nilr₄ and NiOs₄ Alloy Nanoparticles and Their Catalytic Performance in Hydrogenation Reactions

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Abstract. Bimetallic Nilr₄ and NiOs₄ alloy nanoparticles are prepared and studied regarding their performance in catalytic hydrogenation reactions. Nilr₄ and NiOs₄ nanoparticles are obtained via oleylamine-driven reduction and exhibit mean diameters of 8.9±1.3 and 6.8±1.4 nm at low agglomeration. The phase composition was determined in detail based on different methods including HRTEM, STEM, SAED, XRD and EDXS and results in a uniform distribution of both metals Ni-Ir and Ni-Os, with a ratio of 1:4. The catalytic performance of the Nilr₄ and NiOs₄ nanoparticles for hydrogenation reactions is evaluated using three selected model substrates: 1-octene, cinnamaldehyde and diphenylacetylene. Similar sized Ni, Ir, and Os nanoparticles serve as references. Most remarkable are the excellent selectivity of NiOs4 in the hydrogenation of cinnamaldehyde as well as the promising formation of Zstilbene in terms of conversion activity and selectivity. Alloying Ir and Os with Ni, moreover, is highly cost efficient. In general, both bimetallic alloy nanoparticles - Nilr₄ and NiOs₄ - are here first shown in view of synthesis, composition and catalytic hydrogenation.

Introduction

Bimetallic nanoparticles already turned out as highly promising for high efficiency and selectivity in catalysis.^[1] Specific examples, for instance, comprise the systems Fe-Ru for efficient Fischer-Tropsch synthesis,^[2] AI-Fe as Pd-free hydrogenation catalyst,^[3] Rh-Pd for selective CO oxidation,^[4] Pt-Co for renewable fuel generation,^[5] or the activation of gold in bimetallic systems.^[6] Several studies have also demonstrated that bimetallic nanoparticles can outperform their monometallic counterparts.^[2-7] Specific intermetallic interactions in these alloyed or core-shell type systems were postulated to result in synergistic effects. This can include a tuned electronic or geometric structure as well as an improved thermal or chemical stability. As a result, bimetallic nanocatalysts did not only display the combined properties of the pure components but rather exhibit a significantly higher catalytic performance in terms of activity, selectivity, etc.^[2-7] In some cases, the catalytic performance could be improved even if one of the constituents was less active or even inactive for certain reaction.

Most of the yet available multimetallic nanocatalysts are based on precious metals.^[1-7] To this concern, alloying precious metals with an abundant, less-precious metal is of particular interest not only for improving the catalytic properties but also for effective cost reduction.^[8] In contrast to bimetallic *M*-Pd or *M*-Pt systems (*M*: metal), bimetallic systems of iridium and osmium have been barely addressed, in general. Specifically, the system Ni-Ir was yet described for hydrogen generation via electro-

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 Supporting information (characterization methods and synthesis/characterization of reference materials) for this article is available on the WWW under http://dx.doi.org/xxxxx/anie.xxxxxx. catalytic water splitting^[9] or via catalytic hydrazine decomposition,^[10] as well as for catalytic hydrogen oxidation reactions^[11] and ring-opening reactions.^[12] Catalytic hydrogenation with Ni-Ir nanoparticles was yet reported once based on heavily agglomerated nanoparticles that nevertheless already indicate promising conversion rates.^[13] Moreover, pure Ir nanoparticles supported on graphene were employed to effectively catalyze the hydrogenation of benzene to cyclohexane.^[14] Data regarding the catalytic activity of the bimetallic Ni-Os system, to the best of our knowledge, are not available by now. This lack of knowledge motivated us to address the synthesis and characterization of uniform bimetallic Ni-Ir and Ni-Os nanoparticles.

Besides chemical synthesis and structural characterization, the as-prepared bimetallic Ni-Ir and Ni-Os nanostructures were evaluated in view of the catalytic hydrogenation including efficiency and selectivity based on three model substrates. Thus, 1-octene was selected due its low sterical hindrance and simple chemical structure. The second example, cinnamaldehyde, is a cornerstone of catalysis in terms of chemoselectivity since the hydrogenation of α,β -unsaturated aldehydes is particularly challenging due to the high thermodynamic stability of the C=O bond in comparison to the allylic C=C bond. The selective hydrogenation of such allylic aldehydes to unsaturated alcohols, moreover, is commercially relevant in view of flavors and pharmaceutics.^[15] Finally, diphenylacetylene is highly relevant for production of (Z)-/(E)-stilbene, which is an important building block for dyes, liquid crystals, fluorescent whitners, and OLEDs. Usually, synthesis is performed by Wittig or Heck reactions that essentially consume stoichiometric amounts of organic reagents, such as base.^[16] For all three test substrates – 1-octene, cinnamaldehyde - the realization of novel atom-efficient and selective heterogeneous catalyst is highly relevant.

Results and Discussion

Material synthesis

The novel bimetallic NiIr₄ and NiOs₄ nanoparticles were prepared in oleylamine that served as solvent, surface stabilizing agent for controlling particle nucleation and particle growth as well as reducing agent for the reduction of the starting materials to the elemental metals. Thus, NiCl₂x6H₂O and IrCl₃xnH₂O or OsCl₃xnH₂O were used the starting materials and heated to 300 °C. During heating, the change from light green (for Ni-Ir) and reddish-brown (for Ni-Os) solution to dark brown suspensions indicated the successful reduction and nucleation of NiOs₄ and NiIr₄ nanoparticles.

After natural cooling to room temperature, the asprepared bimetallic nanoparticles were purified by repeated centrifugation/redispersion from/in a mixture of hexane and ethyl acetate (ratio 1:3). This measure, especially, intends to separate the removal of oleylamine. Finally, the metal nanoparticles can be easily redispersed in hexane. The synthesis essentially requires the absence of air/oxygen and moisture to avoid any oxidation. Therefore, the synthesis was performed in dried argon atmosphere. It is to be noted that NiOs₄ and NiIr₄

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nanoparticles turned out as stable in air at room temperature subsequent to synthesis.

Interestingly, the compositions Nilr₄ and NiOs₄ were obtained even if the ratio of the starting materials was different from 1:4, which points to a specific stability of the 1:4 phases at the conditions of synthesis. Thus, Nilr₄ and NiOs₄ are obviously most insoluble upon reducing NiCl₂×6H₂O, IrCl₃×nH₂O and OsCl₃×nH₂O in oleylamine. As alloys, their formation can hardly be attributed to a certain stability of the 1:4 compositions. In contrast, a complex equilibrium between the stability of the coordination complexes in solution (i.e. coordination of Ni²⁺, Ir³⁺, Os³⁺ by oleylamine) and the reduction potential of the metals (i.e. reduction of Ni2+, Ir3+, Os3+ by oleylamine) is involved. To this concern, it is to be noted that neither IrCl₃×nH₂O nor OsCl₃×nH₂O can be reduced by oleylamine in the absence of NiCl₂×6H₂O. Thus, the decisive equilibria - including the stability of the dissolved coordination complexes and the redox potential for the formation of elemental metals - have opposing trends resulting in Nilr₄ and NiOs₄ as the most stable phases with the here applied conditions of synthesis.

The reference materials – pure Ni, Ir and Os nanoparticles – were intended to exhibit almost identical particle diameters as the as-prepared bimetallic NiOs₄ and NiIr₄. To this regard, pure Ni was prepared via a similar synthesis route. Pure Ir and Os were not available from oleylamine-based synthesis due to the formation of soluble coordination complexes. Thus, the Ir and Os nanoparticles were obtained via a modified synthesis protocol (see experimental section) with similar size and colloidal stability as NiOs₄ and NiIr₄ (see Table 1; *SI: Figures S1-S4*), and – subsequent to washing – similar surface conditioning (see experimental section).

Nilr₄ nanoparticles

Subsequent to synthesis, the particle size and size distribution of the as-prepared NiIr₄ nanoparticles were characterized by dynamic light scattering (DLS) and electron microscopy. According to DLS, the as-prepared NiIr₄ nanoparticles show a lognormal size distribution with an average hydrodynamic diameter of 10.2±1.3 nm (Figure 1a,b). Low-energy scanning transmission electron microscopy (STEM) overview images support this finding based on a statistical evaluation of 100 nanoparticles with a mean diameter of 8.9±1.3 nm (Figure 1c).

Information regarding structure and composition of the as-prepared Nilr4 nanoparticles was obtained by X-ray diffraction (XRD), selective area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM). Thus, the XRD pattern, together with the corresponding fit and difference plot only show two Bragg peaks that could be detected due to the limited angular aperture of the applied detector (Figure 1d). These peaks are attributed to a single-phase Ni-Ir intermetallic alloy with a face-centered-cubic (fcc) structure (space group Fm-3m). This assessment is supported by the fcc structure of both bulk-Ni and bulk-Ir as well as by the formation of Ni-Ir intermetallic alloys with fcc structure over the whole compositional range.^[17] The here calculated lattice parameter ($a = 0.374 \pm 0.004$ nm) is 3% smaller than for bulk-Ir (a = 0.384 nm) and for the Irreference nanoparticles ($\dot{a} = 0.384 \pm 0.001$). Moreover, XRD line-profile analysis^[18] results in a mean crystallite diameter of 9 nm, which is in good agreement with DLS and STEM. All observed Debye-Scherrer rings on SAED patterns of the nanoparticles can again be attributed to a single-phase Ni-Ir alloy with fcc structure (Figure 1e). From the corresponding azimuthally averaged intensity of the SAED pattern (Figure 1f), a lattice parameter of $a = 0.373 \pm 0.003$ nm was obtained. This finding is in good agreement with XRD and supports a 3% contraction of the lattice as compared to bulk-Ir. It is to be noticed that diffraction peaks of elemental Ir and/or Ni were not observed in XRD and SAED patterns, suggesting the presence of a pure binary Ni-Ir alloy phase.

Figure 1. Nilr₄ nanoparticles: a) Size distribution according to DLS; b) photo of suspension in hexane; c) low-energy STEM overview image; d) indexed XRD pattern (symbols) with whole-pattern-diffraction fit (solid line) and difference plot; e) indexed SAED pattern of nanoparticle ensemble; f) indexed radial scan (symbols) with whole-pattern fit (solid lines) and difference plot, calculated from the SAED pattern in (e); g) HRTEM image of typical Ni-Ir nanoparticle with multiply twinned structure; h) HRTEM image of monocrystalline Ni-Ir nanoparticle; i) diffractogram of the nanoparticle part marked by dashed frame in (h) and calculated diffraction pattern with Miller indices for the *fcc* structure (blue circles).

Whereas the average structure of a quasi-infinite number of particles and of particle aggregates were derived via XRD and SAED, HRTEM allows studying the structure of individual Ni-Ir nanoparticles. Accordingly, lattice fringes extend through the whole nanoparticle and indicate most often monocrystalline structures (Figure 1h) accompanied by few multiply twinned structures (Figure 1g). Monocrystallinity is demonstrated by the good agreement between its 2-dimensional Fourier transformation (denoted in the following as diffractogram) and the calculated *fcc*-type diffraction pattern (a = 0.371 nm, [111] zone-axis orientation) (Figure 1i). A multiply twinned nanoparticle with several, rather small facets and slightly different orientation is shown in Figure 1g. Here, lattice-fringe distances of $d_1 = 0.22 \pm 0.01$, $d_2 = 0.13 \pm 0.01$, $d_3 = 0.13 \pm 0.01$ and $d_4 = 0.19 \pm 0.01$ nm were measured on different facets of the Ni-Ir nanoparticle that correspond to the (111), (220) and (200)



lattice-plane distances ($d_{(111)} = 0.214$, $d_{(220)} = 0.131$, $d_{(200)} = 0.186$ nm). Again, for both – monocrystalline and twinned nanoparticles – the lattice parameters (a = 0.371 nm) derived from the nanoparticle diffractogram are 3% smaller than the corresponding value of bulk-Ir.^[17]

EDXS area scans were used to determine the average chemical composition of the Ni-Ir nanoparticles (Figure 2a,b) and show the characteristic lines of Ni-K and Ir-L series (lines of Cu-K series stem from the grid). The quantification of the Ni and Ir content within the Ni-Ir nanoparticle in Figure 2a yielded 20±2 at-% Ni and 80±1 at-% Ir. Furthermore, an average chemical composition of $Ni_{21\pm2}Ir_{79\pm3}$ was obtained from EDXS area scans of 60 Ni-Ir nanoparticles located in different regions on the sample. Moreover, EDXS line-profiles indicate a uniform Ni and Ir distribution and again an average composition of 19±2 at-% Ni and 81±2 at-% Ir (Figure 2c,d). Finally, powder samples were pressed to pellets and studied via EDXS (see SI). Again, a 1:4 ratio of Ni and Ir was detected (SI: Table S1) and, in sum, confirms the composition and homogeneity of Nilr4 for individual nanoparticles as well as for powder samples.

In conclusion, single-phase Ni-Ir alloy nanoparticles with *fcc* structure and uniform chemical composition NiIr₄ were obtained as indicated by the above independent analytical tools (XRD, SAED, HRTEM, EDXS). The formation of a single-phase Ni-Ir intermetallic alloy rationalizes the contraction of the *fcc* lattice parameter of the nanoparticles. A decrease of the lattice parameter value is indeed expected after dissolving Ni (*r*_{Ni} = 0.124 nm) in the structure of Ir (*r*_{Ir} = 0.136 nm).^[19]



Figure 2. NiIr₄ nanoparticles: a) HAADF-STEM image with b) area-EDX spectrum (dashed box area in (a)); c) HAADF STEM image with d) Ni and Ir composition profiles (along orange line in (c)).

Ni-Os nanoparticles

According to DLS, the as-prepared NiOs₄ nanoparticles exhibit a narrow log-normal particle distribution with an average hydrodynamic diameter of 8.2±1.2 nm (Figure 3a,b). Low-energy STEM and TEM overview images indicate a mean particle diameter of 6.8±1.4 nm (based on a statistical evaluation of 100 nanoparticles, Figure 3c,d). According to XRD, the Ni-Os nanoparticles adopt a hexagonal-close-packed (*hcp*) structure (space group *P6₃/mmc*) with lattice parameters of *a* = 0.260±0.003 and *c* = 0.427±0.004 nm (Figure 3e,f). Thus, a contraction of 5% (for *a*) and 2% (for *c*) was observed in comparison to bulk-Os (*a* = 0.274, *c* = 0.432 nm). An average crystallite diameter of 7 nm

was calculated by single XRD line-profile analysis,^[18] which is well in agreement with DLS and STEM.

SAED patterns confirm the XRD results (Figure 3f). All observed Debye-Scherrer rings are in accordance with the sole presence of a Ni-Os alloy with *hcp* structure. The azimuthally averaged SAED pattern as well as the corresponding whole-pattern fit and the difference plot (Figure 3f,g) result in lattice parameters of $a = 0.261\pm0.003$ and $c = 0.423\pm0.004$ nm that confirm the *hcp* structure and the contracted lattice parameters (5% in *a* and 2% in *c*). We also note that Bragg reflections of elemental Ni and/or Os are not observed in the XRD and SAED patterns.



Figure 3. NiOs₄ nanoparticles: a) Size distribution according to DLS; b) photo of suspension in hexane; c,d) low-energy STEM and TEM overview images; e) indexed XRD pattern (symbols) with wholepattern-diffraction fit (solid line) and difference plot; f) indexed SAED pattern of nanoparticle ensemble; g) indexed radial scan (symbols) with whole-pattern fit (solid lines) and difference plot, calculated from SAED pattern in (f); h) typical HRTEM image; i) experimental diffractogram of nanoparticle in (h) with calculated diffraction pattern and Miller indices for *hcp* structure (blue circles). For legibility reasons, not every reflection is marked and explicitly indexed in the diffractogram. The indices of all other reflections can be calculated from the low-indexed reflections. The white circle indicates the zero-order beam (ZB).

Size, shape and structure of the as-prepared Ni-Os nanoparticles were further studied in detail by HRTEM analysis (Figure 3h). Lattice fringes extend through the whole nanoparticle and indicate its crystallinity. Diffractogram and calculated diffraction pattern are in very good agreement with a *hcp* structure (P6₃/mmc, a = 0.259, c = 0.419 nm, along the [211] zone axis, Figure 3i). Again the lattice parameters *a* and *c* are contracted

EDXS area scans reveal the characteristic X-ray lines of the Ni-K and Os-L series (lines of Cu-K series stem from the grid) (Figure 4a,b). Quantification of the Ni and Os content of the nanoparticle in Figure 4a resulted in 20±2 at-% Ni and 80±2 at-% Os. An average chemical composition of Ni_{19±2}Os_{81±3} was derived from EDXS area scans of 110 Ni-Os nanoparticles from different regions of the sample. Moreover, Ni- and Os-concentration profiles from EDXS line scans show a uniform distribution of both (Figure 4c,d) across the selected Ni-Os metals nanoparticle as well as a similar composition (21±2 at-% Ni, 79±2 at-% Os) as obtained from the area scans. Finally, powder samples were pressed to pellets and studied via EDXS (see SI), again resulting in a 1:4 ratio of Ni and Os (SI: Table S1). Accordingly, any segregation of elemental Ni and/or Os can be excluded.

Similar to the Ni-Ir alloy nanoparticles, the Ni-Os nanoparticles can be considered as single-phase alloy nanoparticles with a uniform chemical composition of NiOs₄. Structure and composition are reliably determined based on independent analytical tools (XRD, SAED, HRTEM, EDXS). The Ni-Os alloy formation explains well the 5% and 2% contraction of the a and c lattice parameters for alloyed Ni-Os nanoparticles as compared to the corresponding bulk-Os as well as the Os-reference nanoparticles (a = 0.274±0.001, c = 0.433±0.001 nm). A decrease of the a and c lattice parameter values is indeed expected after dissolving Ni (r_{Ni} = 0.124 nm) in the structure of Os (r_{Os} = 0.135 nm).^[20] In fact, the here obtained NiOs₄ composition is surprising since the maximum Ni content in Ni-Os phases reaches only 13 at-% (at 1500 °C) according to the peritectic equilibrium phase diagram. $^{\rm [20]}$ Moreover, the maximum Ni content was reported to decrease even further at lower temperature reaching 11.2 at-% at 1400 °C and 9.2 at-% at 1200 °C, respectively.^[20] With 20 at-% Ni the here prepared NiOs4 nanoparticles, altogether, represent a new alloy, whose formation can be ascribed to the lowtemperature synthesis with kinetic reaction control.

Altogether, the nanoparticles – NiIr₄, NiOs₄ as well as the Ni, Ir and Os references – exhibit comparable mean diameters (5-10 nm) and very narrow size distributions. Hereof, the NiIr₄, NiOs₄ and Ni nanoparticles are slightly larger (8-9 nm) as compared to the Ir and Os nanoparticles (3-4 nm). An overview of diameters and the relevant discussion is given in Table 1 and the Supporting Information (*SI: Figures S1-S4*).



Figure 4. NiOs₄ nanoparticles: a) HAADF-STEM image with b) area-EDX spectrum (dashed box area in (a)); c) HAADF-STEM image with EDX line-scan with d) Ni and Ir composition profiles (along orange line in (c)).

Table 1. Mean diameter of the as-prepared NiIr₄ and NiOs₄ nanoparticles as well as of the Ni, Ir, and Os reference nanoparticles (according to DLS and TEM analysis).

Nanoparticles	Mean diameter (DLS) [nm]	Mean diameter (TEM) [nm]
Nilr ₄	10.2±1.3	8.9±1.3
NiOs ₄	8.2±1.2	6.8±1.4
Ni	10.4±1.4	8.7±0.9
lr	5.1±0.6	3.7±0.9
Os	5.2±0.5	3.9±1.4

Catalytic hydrogenation with Nilr₄ and NiOs₄ particles

For further evaluation of the alloyed bimetallic Nilr₄ and NiOs₄ nanoparticles, we tested the catalytic activity and selectivity in hydrogenation reactions for three unsaturated substrates (i.e., 1-octene, cinnamaldehyde and diphenylacetylene). For all catalytic experiments, the as-prepared nanoparticles were employed as suspensions in hexane (1.5-3.0 mL). Although the partial formation of agglomerates cannot be completely excluded, the atoms located at the particle surface should be, in principle, accessible to interact with the substrates. Hence, turnover frequencies based on surface atoms (TOF_s) were estimated by calculating the ratio of the number of surface atoms to the total number of atoms based on the mean diameters (i.e., as obtained from TEM images, Table 1) and used to evaluate the catalytic properties of the Nilr₄ and NiOs₄ nanoparticles. Nanoparticles of Ni, Ir, and Os were used as references. These reference nanoparticles show very comparable particle sizes, colloidal stability and surface conditioning (Table 1; SI: Figures S1-S4; see Experimental Section). These are crucial aspects in view of direct comparison of the catalytic performance.

Nilr₄ and NiOs₄ nanoparticles were first tested for their catalytic activity in hydrogenation reactions using 1-octene as a linear, terminal olefin with a sterically non-hindered C=C bond (Figure 5a). The reaction was carried out at room temperature and 10 bar H₂ pressure. The H₂ consumption was continuously recorded. Both bimetallic nanoparticles, Nilr₄ and NiOs₄, turned out as active catalysts, resulting in TOF_s (after 3 h of reaction) of 5025 (Nilr₄) and 313 h⁻¹ (NiOs₄) (Table 2). Thus, Nilr₄ turned out as much more active as compared to NiOs₄. Figure 5b displays the H₂ uptake over time for the hydrogenation of 1-octene with Nilr₄ nanoparticles.

Table 2. Hydrogenation of 1-octene using NiIr₄ and NiOs₄ nanoparticles (at room temperature, 10 bar H_2).

Nanoparticles	Substrate [mol]	Conversion [%]	Time [h]	TOF _s [h ⁻¹]	-
Nilr ₄ (30 mg)	0.13	100	14	5025	-
NiOs ₄ (20 mg)	0.09	89	24	313	
Ni (10 ma)	0.06	100	14	1131	

We further employed cinnamaldehyde (CAL) as a model compound to study the selective hydrogenation of α,β -unsaturated carbonyls. The selective hydrogenation of unsaturated carbonyl compounds is a critical step in the synthesis of various fine chemicals, in particular, in the flavor, fragrance or pharmaceutical chemistry.^[15] Instead of the desired, unsaturated alcohols, however, the saturated aldehydes are the thermodynamically favored products due to the higher free reaction enthalpy of C=O (40 kJ/mol) compared to C=C (35 kJ/mol). Therefore, efforts have been directed to enhance the selectivity for the unsaturated alcohol, e.g., by additives, allovs. stabilizers, ligands, or metal-support interactions.^[14] The hydrogenation of CAL proceeds via different reaction pathways and stepwise hydrogenation of the C=C or C=O bond to the intermediate saturated aldehyde (i.e., hydrocinnamic aldehyde, HCAL) or the unsaturated alcohol (i.e., cinnamic alcohol, CAOL),

accordingly, to the saturated alcohol (i.e., hydrocinnamic alcohol, HCAOL) (Figure 6a). In general, the unpromoted pure metals Os and Ir were previously reported to exhibit high selectivities to the unsaturated alcohol CAOL, while pure Ni is known as rather unselective.^[15] Recently, intermetallic Ni-In or alloyed Ni-Sn catalysts were described for the selective hydrogenation of unsaturated carbonyls.^[21]



Figure 5. Hydrogenation of 1-octene: a) Scheme of reaction sequence; b) Time-dependent H_2 gas uptake with Nilr₄ nanoparticles (at room temperature, 10 bar H_2).



Figure 6. Hydrogenation of cinnamaldehyde (CAL): a) Scheme of reaction sequence; b) Time-dependent CAOL yield in the hydrogenation of CAL with Nilr₄ nanoparticles using different reaction media (methanol, 2-propanol, THF; at 80 °C, 10 bar H₂).

The catalytic hydrogenation of CAL with the NiIr₄ and NiOs₄ nanoparticles as well as with the Ni, Ir and Os references was investigated at a pressure of 10 bar H₂ and 80 °C using various reaction media (i.e., methanol, 2-propanol, THF). The results of the catalytic experiments are summarized in Table 3. The choice of the solvent was shown to affect both the catalytic behavior of the nanoparticles and the formation of by-products. An effect of the solvent on the catalytic activity was also observed by others. Thus, Iow activities were described for hydrocarbons, whereas high activities were reported for light alcohols (e.g., methanol, ethanol, 2-propanol).^[14,18] In our experiments, the highest activity and yield in CAOL were obtained, if methanol was employed as reaction

medium (Figure 6b). In methanol, however, the formation of acetals as by-products was favored, even in the catalyst (Figure 7). absence of the Significant acetalization (i.e., the formation of hemiacetal and acetal products) was previously reported by others, e.g., in the hydrogenation of furfural due to the reaction of the solvent (i.e., alcohols such as methanol, ethanol or isopropanol) and the aldehyde, even in absence of the Ni catalyst. $\ensuremath{^{[22]}}$ It was also reported that alcohol can serve as a hydrogen reactions.[23] hydrogen source transfer in Gaschromatographic (GC) analysis, on the other hand, showed that the formation of acetals is reversible. Hence, the acetals were here completely converted into reaction products (i.e., HCAOL, CAOL, CAL) after a sufficiently long reaction time. Lower amounts of acetals were formed, if 2-propanol was used instead of methanol (Table 3). After 22 h of reaction, only the reaction products and no acetals were determined by GC analysis. However, the use of 2-propanol instead of methanol considerably reduced both the catalytic activity and the CAOL yield in the case of the Nilr₄ and NiOs₄ nanoparticles (Figure 7). In THF, where obviously no acetals could be formed, the hydrogenation of the C=C bond was favored over the hydrogenation of the C=O bond, and HCAL was formed as the main product (Table 3).

Table 3. Hydrogenation of cinnamaldehyde (CAL) using NiIr₄ and NiOs₄ nanoparticles (Ni, Os and Ir nanoparticles as references; at 80° C, 10 bar H₂; reaction time 3 h; unless specified otherwise).

Cat	CAOL yield	Product	Product selectivity [%]			
out.	[%]	CAOL	HCAOL	HCAL	Other ^e	[h ⁻ ']
$\operatorname{Nilr_4}^{\mathrm{a}}$	19	23	2	3	72	419
${\sf NiOs_4}^{\sf a}$	11	28	1	5	66	158
Ni ^a	2	3	19	19	59	150
Ir ^a	14	22	3	2	73	675
Os ^b	48	52	22	12	14	952
Nilr4 ^c	2 9 ^f	27 60 ^f	0 7 ^f	0 33 ^f	73 0 ^f	35 10 ^f
NiOs4 ^c	1 6 ^f	50 61 ^f	0 0 ^f	0 39 ^f	50 0 ^f	5 3 ^f
Nilr4 ^d	1	28	12	60	0	25

^{a.c}20 mg; ^b24 mg; or ^d10 mg of the nanoparticle powder was suspended in 1.5-3.0 mL hexane and used as catalyst. Substrate and solvent: ^{a.b}CAL (16 mmol) in 30 mL methanol; ^cCAL (16 mmol) in 30 mL 2-propanol; ^dCAL (8 mmol) in 15 mL THF; ^eOther: Acetals (hemiacetal, unsaturated/saturated acetals); ^fReaction time 22 h.



Figure 7. Product selectivity in the hydrogenation of CAL with bimetallic NiIr4 and NiOs4 nanoparticles and their monometallic Ir, Os and Ni counterparts (at 80 °C, 10 bar H₂; reaction time: 3h; solvent: methanol). Acetals (i.e., unsaturated/saturated hemiacetals or acetals) were formed as byproducts (i.e., others).





Figure 8. Time-depending selectivity in the hydrogenation of CAL with a) NiIr₄ and b) NiOs₄ nanoparticles (at 80 $^{\circ}$ C, 10 bar H₂, solvent methanol).

The highest yield in CAOL (i.e., 48% after 3 h) was obtained for the Os-based nanocatalysts. In general, alloying Ir and Os with Ni in the bimetallic NiIr₄ and NiOs₄ particles, respectively, resulted in a decrease of the TOFs from 675 (Ir) and 952 h⁻¹ (Os) to 419 (Nilr₄) and 158 h⁻¹ (NiOs₄). Alloying Os with Ni in the NiOs₄ nanoparticles reduced the CAOL yield considerably to 11%. However, almost no HCAOL (1%) was formed in the case of the NiOs₄ nanoparticles as compared to the pure Os nanoparticles (22%). In the case of the Ir-based nanoparticles, a different behavior was observed. Alloying of Ir with Ni lead to an increase in the CAOL yield ranging from 14% for the pure Ir nanoparticles (3 h) to 16% for the bimetallic Nilr₄ nanoparticles (3 h) (Table 2). This is even more remarkable since the pure Ni nanoparticles - as expected - were rather selective for the formation of HCAOL with a low yield in CAOL (2%). Figure 8 shows the time course of the selectivity for the alloyed Nilr₄- and NiOs₄-based catalysts. In terms of direct comparison, moreover, it is to be noted that - although synthesis was adapted on as far as possible similar particle sizes - the reference Ir and Os reference nanoparticles are smaller (3-4 nm) than the bimetallic Nilr₄ (9 nm) and NiOs₄ (7 nm) nanoparticles (Table 1). In terms of size and active surface area, thus, the reference nanoparticles have the edge over the novel Nilr₄ and NiOs₄ nanoparticles.

Finally, the selective hydrogenation of alkynes with the alloyed NiIr₄ and NiOs₄ nanoparticles was studied using diphenylacetylene (DPA) as a probe substrate. DPA can be hydrogenated over (Z)- or (E)-stilbene to 1,2diphenylethane (DPE) (Figure 9a). (Z)-/(E)-stilbene are interesting building blocks for dyes, liquid crystals, fluorescent whitener and OLEDs.^[19] In general, Pd-based bimetallic catalysts (e.g., Lindlar catalyst) were employed for the semihydrogenation of alkynes to alkenes.^[24] has been recently shown to selectively hydrogenate DPA to (E)-stilbene.^[25] Several, non-precious alloyed catalysts have been also identified for the selective gas phase hydrogenation of acetylene.^[3,26] Recently, Ni nanoparticles in ionic liquids have been reported as selective nanocatalysts for the semihydrogenation of alkynes to (Z)-alkenes.^[27]



Figure 9. Hydrogenation of diphenylacetylene (DPA): a) Scheme of reaction sequence; b) Time-depending conversion and selectivity in the hydrogenation of DPA using the NiOs₄ nanoparticles (at 80 °C, 10 bar H_2 , solvent: THF).

Here, the catalytic tests with Nilr₄ and NiOs₄ were carried out at 80 °C and 10 bar H₂ using THF as a reaction medium (Table 4, Figure 9b).^[20] After a reaction time of 1 h, the conversion was 7 and 45% for the Nilr₄ and NiOs₄ nanoparticles, respectively, in comparison to 9% for the Ni reference (Table 4). The resulting, TOF_s were 35 (Nilr₄), 110 (NiOs₄) and 21 h⁻¹ (Ni). Thus, the values are decreasing from NiOs₄ over Nilr₄ to the monometallic Ni nanoparticles. (Z)-stilbene was the main product for all nanocatalysts; the yield in (Z)-stilbene after 1 h was 38% for NiOs₄, but remained low for Nilr₄ (5%) and Ni (6%). As a conclusion, NiOs₄ is promising for obtaining Z-stilbene in terms of conversion, selectivity and TOF.

Table 4. Hydrogenation of DPA with bimetallic NiOs₄ and NiIr₄ nanoparticles (Ni nanoparticles as a reference; at 80°C, 10 bar H₂, 30 mL THF, 20 mg nanoparticle powder).

Cat.	Conversion [%]	Time [h]	Product selectivity [%]			TOF₅
			(Z)- stilbene	(E)- stilbene	DPE	[h ⁻¹]
Nilr ₄	7	1	67	23	10	35
NiOs ₄	45	1	85	5	10	110
Ni	9	1	71	19	10	21

Conclusion

Bimetallic Nilr₄ and NiOs₄ nanoparticles were prepared via oleylamine-driven reduction and exhibit mean diameters of 8.9 ± 1.3 and 6.8 ± 1.4 nm at low degree of agglomeration. Particle size and phase composition were determined in detail by different analytical methods including HRTEM, STEM, SAED, XRD and EDXS. Accordingly, both nanoparticles exhibit a homogeneous distribution of Ni-Ir and Ni-Os with a ratio of 1:4. The bimetallic alloy nanoparticles Nilr₄ and NiOs₄ are presented for the first time, which is especially remarkable for NiOs₄ since the bulk system Ni-Os exhibits a miscibility gap for such high Ni contents.

To evaluate the catalytic properties of the novel Nilr4 and NiOs₄ nanoparticles, we have studied their catalytic activity and selectivity in hydrogenation reactions using selected model substrates (i.e, three 1-octene. cinnamaldehyde and diphenylacetylene). Nanoparticles of pure Ni, Ir, and Os with similar particle size and colloidal stability were used as references. Both types of alloyed particles – Nilr₄ and NiOs₄ – are first shown in view of catalytic hydrogenation. Typically, the Nilr₄ and NiOs₄ nanoparticles show a higher activity and selectivity than the pure Ni reference. Whereas the Nilr₄ nanoparticles except for optional cost reduction - do not exhibit a specific advantage in comparison to pure Ir, the NiOs4 nanoparticles show promising features for the hydrogenation of cinnamaldehyde and diphenylacetylene. Although alloying Os with Ni in NiOs₄ nanoparticles lead to a decrease in both the yield of cinnamic alcohol and the activity, a significantly increased selectivity for the hydrogenation of the C=O bond to cinnamic alcohol was achieved. Moreover, almost no hydrocinnamic alcohol was formed in the presence of NiOs₄. Interestingly, intermediate acetals were completely converted into useful products after sufficiently long reaction time. Besides the selective hydrogenation of cinnamaldehyde, NiOs₄ turned out as promising for obtaining Z-stilbene in terms of conversion, selectivity and TOF.

Besides the promising selectivity of NiOs₄, alloying the precious metals (i.e., Ir, Os) with a common, inexpensive base metal (i.e., Ni) at identical activity is beneficial in terms of cost reduction. As the choice of the solvent was shown to affect both the catalytic activity as well as the selectivity, further improvement has to address not only the catalyst itself but also the specific experimental conditions (e.g., pressure, reactant concentrations). In sum, the selectivities remained overall high after alloying, which may open up interesting possibilities in view of the development of cost effective bimetallic catalytic systems.

Experimental section

Material synthesis

General aspects. All reactions were performed under dynamic nitrogen purging. Purification and analysis were performed under ambient atmosphere. Nickel(II)chloride hexahydrate (97 %, Riedel de Haën); iridium(III)chloride hydrate (99.9 %, ABCR); osmium(III)chloride hydrate (black xtl., ABCR); oleylamine (80-90 %, Acros); ethylene glycol (extra pure, Riedelde Haën). For better handling osmium(III)chlorid hydrate was pestled and thereafter dried in vacuum for two hours.

Nilr₄ nanoparticles. 60 mg NiCl₂x6H₂O and 149 mg IrCl₃xnH₂O were dissolved in 20 mL of oleylamine. The solution was heated to 100 °C and stirred for 60 minutes in order to remove moisture and oxygen. Thereafter, the reaction mixture was heated to 300 °C with a heating rate of 26 K/min and kept at this temperature for 10 minutes. Thereby, the color of the mixture changed from light green to dark brown. After natural cooling to room temperature about 30 mL of ethyl acetate were added to the product suspension followed by centrifugation. The black precipitate was washed two times with a 1:3 mixture of hexane

and ethyl acetate. The product can be easily redispersed in hexane.

 $NiOs_4$ nanoparticles. 60 mg NiCl₂x6H₂O and 74 mg OsCl₃xnH₂O were dissolved in 20 mL of oleylamine. The solution was heated to 100 °C and stirred for 60 minutes in order to remove moisture and oxygen. The color of the solution changed from dark reddish-brown to dark blue. Thereafter, the reaction mixture was heated to 300 °C with a heating rate of 26 K/min and kept at this temperature for 30 minutes. Thereby, the color of the mixture changed to dark brown. After natural cooling to room temperature about 30 mL of ethyl acetate were added to the product suspension followed by centrifugation. The black precipitate was washed two times with a 1:3 mixture of hexane and ethyl acetate. The product can be easily redispersed in hexane.

Ni nanoparticles (reference). 140 mg NiCl₂x6H₂O were dissolved in 20 mL of oleylamine. The solution was heated to 100 °C and stirred for 60 minutes in order to remove moisture and oxygen. Thereafter, the reaction mixture was heated to 300 °C with a heating rate of 26 K/min and kept at this temperature for 10 minutes. Thereby, the color of the mixture changed from green to dark brown. After natural cooling to room temperature about 30 mL of ethyl acetate were added to the product suspension followed by centrifugation. The black precipitate was washed two times with a 1:3 mixture of hexane and ethyl acetate. The product can be easily redispersed in hexane.

Ir nanoparticles (reference). 80 mg IrCl₃xnH₂O and were dissolved in 20 mL of ethylene glycol. The solution was heated to 150 °C with a heating rate of 20 K/min and kept at this temperature for 60 minutes. The color of the solution changed from yellowish to dark brown. After natural cooling to room temperature about 30 mL of ethanol were added to the product suspension followed by centrifugation. The black precipitate was washed two times with ethanol. The product can be redispersed in Hexan.

Os nanoparticles (reference). 80 mg OsCl₃×nH₂O and were dissolved in 20 mL of ethylene glycol. The solution was heated to 150 °C with a heating rate of 20 K/min and kept at this temperature for 60 minutes. The color of the solution changed from yellowish to dark brown. After natural cooling to room temperature about 30 mL of ethanol were added to the product suspension followed by centrifugation. The black precipitate was washed two times with ethanol. The product can be redispersed in Hexan.

Analytical methods

Dynamic light scattering (DLS) was performed with a Nanosizer ZS from Malvern Instruments (equipped with a He-Ne laser (633 nm)), detection via non-invasive back-scattering at an angle of 173°, 256 detector channels, polystyrene cuvettes). For analysis, the as-prepared nanoparticles were redispersed in hexane. The obtained size distributions can be well fitted with lognormal distribution functions.^[28]

Scanning electron microscopy (SEM) was performed on a Zeiss Supra 40 VP at an acceleration voltage of 20 kV and a working distance of 3 mm, while for *low-energy scanning transmission electron microscopy (STEM)* an acceleration voltage of up to 30 kV and a working distance of 4 mm was used. The samples were prepared on holey carbon-film copper-grids by evaporating a single drop of a dispersion of as-prepared nanoparticles in hexane at room temperature in air. *Energy-dispersive X-ray (EDX) analysis* was performed with an Ametek EDAX device mounted on the above described Zeiss SEM Supra 40 VP scanning electron microscope. For this purpose, powder samples (300 mg) were pressed (50 tons) to dense pellets in order to guarantee for a smooth surface and a quasi-infinite layer thickness. These pellets were fixed with conductive carbon pads on aluminum sample holders.

High-resolution (HR) transmission electron microscopy (TEM) and high-angle annular dark-field (HAADF) STEM are conducted with an aberration-corrected FEI Titan³ 80-300 microscope at 300 kV. The experiments were performed with the same samples that were used for overview STEM images. Alternatively, HRTEM images were evaluated by calculating the 2-dimensional Fourier transformation – denoted as diffractogram – which yielded information on the crystal structure (lattice parameters and crystal symmetry) of single nanoparticles. *Selected-area electron diffraction (SAED)* patterns of nanoparticle ensembles were taken with a Philips CM 200 FEG/ST microscope at 200 kV to investigate their crystal structure. Further information can be obtained from the Supporting Information.

The chemical composition of single nanoparticles was investigated by *energy-dispersive X-ray spectroscopy (EDXS)* performed with the FEI Titan³ 80-300 microscope at 300 keV electron energy by using an EDAX Si(Li) detector. EDX spectra are quantified with the FEI software package "TEM imaging and analysis" (TIA) version 3.2. Using TIA, element concentrations were calculated on the basis of a refined Kramers' law model, which includes corrections for detector absorption and background subtraction. Further information can be obtained from the Supporting Information.

X-ray powder diffraction (XRD) analysis was carried out on a Stoe Stadi-P diffractometer using Cu-K_{a1} radiation ($\lambda = 0.1540598$ nm) monochromated by a focusing Ge crystal. A position sensitive detector [Stoe IP-PSD, 70 °(20) angular aperture] was used to record the XRD patterns with a step size of 0.03 °(20). The detector channels were calibrated with the line-positions of a Si standard. Further information can be obtained from the Supporting Information.

Thermogravimetry (TG) measurements were performed with a NETZSCH STA 449 F3 applying α -Al₂O₃ as crucible material. The samples were heated under N₂ flow to 1400 °C with a heating rate of 5 °C/min.

Catalytic experiments

Hydrogenation reactions were carried out in a stainless steel autoclave (200 mL). The autoclave was equipped with a telfon inlay, a mechanical blowing stirrer (teflon) and baffles (stainless steel) to achieve intimate mixing between the gas and the liquid phase, a thermocouple and a heating bath. The catalyst and the organic substrate were loaded in the autoclave under argon atmosphere. Dry solvents were used in all catalytic experiments.

In a typical experiment, the nanoparticles were dispersed in hexane (3-5 mL) using an ultrasonic bath, mixed with the organic substrate and added to the autoclave reactor. After heating the mixture to the reaction temperature, the stirrer was started (1200 rpm). The reaction was initiated by introducing hydrogen into the reactor. During catalytic experiments, the hydrogen pressure was kept constant at 10 bar and hydrogen was continuously supplied to the reactor by a gas burette (500 mL, Parr). The consumption of hydrogen was recorded automatically based on the pressure drop in the gas burette. The selectivity and conversion in the hydrogenation of cinnamaldehyde and diphenylacetylene were determined by a flame ionization detection gas chromatograph (GC-FID, Agilent) equipped with a SCIENTIFIC ĎB5 J&W column (Agilent Technology, 30 m×0.25 mm, 0.25 µm film thickness) and a Stabilwax-Da column (30 m×0.25 mm, 0.25 µm film thickness), respectively.

The determination of the turn over frequency (TOF) requires the quantitative determination of the number of active centers of the catalyst, which is typically not a simple task for heterogeneous catalysts or nanoparticles.^[29] Therefore, the TOF of heterogeneous catalysts or nanoparticles have been often related to the total amount of the active phase (moles of metal used) or its surface area. Typically, only the atoms exposed on the nanoparticle surface (or a fraction of them) are catalytically active. In our experiments, the TOF based on surface atoms (TOF_s) were calculated according to equation (1) and used to compare the catalytic performance of the nanoparticle catalysts. The total average atom number (N_T) and the number of surface atoms (N_s) were calculated using the average nanoparticle diameter obtained by TEM analysis.^[30]

 $TOF_{S} = \frac{conversion (\%) * n_{0,CAL}(mol)}{n_{metal/catalyst}(mol) * \frac{N_{S}}{N_{T}} * time(h)} 10^{-2}$ (1)

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Keywords: Nilr₄ • NiOs₄ • Nanoparticle • Hydrogenation • Cinnamaldehyde • Diphenylacetylene

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Entry for the Table of Contents

FULL PAPER

Bimetallic is more selective than monometallic – The bimetallic Nilr₄ and NiOs₄ alloy nanoparticles are first studied and show promising catalytic performance in hydrogenation reactions.



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Bimetallic Nilr₄ and NiOs₄ A Nanoparticles and their Cata Performance in Hydrogena Reactions