

# Nickel Boosts Ring-Opening Activity of Iridium

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A variety of bimetallic Ni–Ir catalysts were synthesised by preforming nanoparticles in the presence of polyvinylpyrrolidone, followed by deposition on  $\gamma$ -alumina and high-temperature polymer removal. The Ni–Ir (1:1 molar ratio) nanoparticles prepared by the hydrogen-sacrificial technique (Ir reduction on the preformed Ni nanoparticles with surface Ni hydride) allowed increasing indane ring opening activity per total amount of Ir as compared to monometallic Ir. The simultane-

### Introduction

Catalytic ring opening (RO) is one of the key processes of increasing the quality of heavy polyaromatic and naphthenic compounds. During the process, a C–C bond on the ring is cleaved only once, leaving the number of carbon atoms in the product unchanged.<sup>[1]</sup> RO increases the volume of the products, and if substituted C–C bonds are the ones cleaved, it can also improve the cetane number. These are two important incentives for the oil market.<sup>[2]</sup>

Since the 1970s, RO of cyclic compounds has been studied extensively using the Pt-group supported catalysts.<sup>[1,3-7]</sup> The RO of naphthenic rings relies on a metal-driven chemistry and among the different metals studied, Ir is the most selective and active ring-opening catalyst.<sup>[1,8,9]</sup> The RO of several cyclic molecules such as methylcyclopentane, ethylcyclopentane, methylcyclohexane, dimethylcyclopentane, dimethylcyclohexane, indane, decalin, perhydroindane and trimethylcyclohexane has been studied using Ir-supported catalysts.<sup>[1,2,5-7,10-14]</sup> Mechanism of the metal-catalysed RO of naphthenic rings depends on the nature of the metal, its particle size, and support effects.<sup>[8,15]</sup> Iridium is reported to operate mostly through the dicarbene mechanism, implying perpendicular adsorption of two carbon atoms of a naphthenic ring, which results in the cleavage of unsubstituted secondary-secondary carbon atom bonds.<sup>[15]</sup> The particle size effect in changing the mechanism of RO is reportedly less pronounced for  $Ir_{t}^{[16, 17]}$  as contrary to the platinum.<sup>[17, 18]</sup> A study of the support effects in the RO of 1,3dimethylcyclohexane revealed that Ir/SiO<sub>2</sub> is selective towards expected unsubstituted C-C bond cleavage, whereas Ir/Al<sub>2</sub>O<sub>3</sub> presented also a significant selectivity for RO at substituted po-

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 Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201300844. ous reduction of Ni and Ir precursors was not as efficient. The catalysts were characterised with UV/Vis spectroscopy, TEM, temperature-programmed reduction,  $CO_2$  temperature-programmed desorption, CO diffuse reflectance Fourier transform spectroscopy, X-ray photoelectron spectroscopy and CHN analysis. The study only explored the catalyst's metal function and allows saving rare and expensive iridium without loss of its outstanding performance as a ring-opening catalyst.

sitions; this unusual behaviour was attributed to be the effect of support rather than the particle size.<sup>[13]</sup>

However, Ir is one of the rarest elements on earth, a concern for the sustainable development. Is there a way to spare the metal without losing its outstanding catalytic performance? Could we place a much more inexpensive metal in the metal nanoparticle core, surrounded by only one layer of the expensive active noble metal, which would make all its atoms available for catalysis? Not with traditional preparation techniques for heterogeneous catalysts. Such techniques, such as impregnation, exert limited control over particle size, particle structure and vicinity between the two metals.<sup>[19]</sup>

The controlled synthesis of bimetallic core-shell nanoparticles, developed about a decade ago, presents an attractive solution.<sup>[20]</sup> Colloid chemistry methods have synthesised bimetallic nanoparticles in a successful, controlled way in recent years, into various structures such as "random alloy" and "coreshell".<sup>[21]</sup> A significant number of core-shell nanoparticles for catalytic applications have remained in the noble-metal region: Au-Pd, Pd-Pt, Ru-Pt, Rh-Pt, Ir-Pt, Au-Pt, Au-Rh and Pd-Ir.<sup>[22-30]</sup> Recent metal cores have comprised cheaper elements such as Ni, Co and Cu to prevent the waste of precious metals at bulk positions. However, to the best of our knowledge, synthesised nanoparticles have only been applied in low temperatures (rarely exceeding 120°C), or synthesised by using relatively complicated methods. Some examples include a series of Co-M (M=Pd, Pt and Au) nanoparticles prepared by colloid chemistry (redox-transmetallation),<sup>[31]</sup> Ni-Pt and Ni-Pd nanoparticles synthesised by wet chemistry (polyol reduction) as the catalysts of proton-exchange membrane fuel cells (operating typically at 50-100 °C) or direct methanol fuel cells (90–120  $^{\circ}\text{C}),^{\scriptscriptstyle[32,33]}$  polyol-assisted synthesis of Ni/Pd for hydrogenation of nitrobenzene to aniline at 27 °C,<sup>[34]</sup> Co/Pt nanoparticles prepared by wet chemistry (redox-transmetallation) for hydrogenation of several compounds at room temperature,<sup>[35]</sup> Ni/Pd nanoparticles synthesised by combined electrochemistry and wet chemistry methods, tested in a cross-coupling reaction at 65 °C,<sup>[36]</sup> and Cu/Pt nanoparticles synthesised by electrodeposition of Cu on carbon electrode followed by Pt shell formation, used in a study of proton-exchange membrane fuel cell catalysts.<sup>[37]</sup>

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The goal of the work was to replace a portion of rare and expensive Ir with the more abundant and less expensive Ni, without incurring any loss in catalytic performance per total Ir loading in a reactor. Indane ring opening was used as a model reaction, representing one of the routes in large-scale industrial fuel upgrading processes. Herein we report the synthesis of bimetallic nanoparticles of Ni and Ir either through simultaneous reduction of metal precursors in the presence of the stabilising polymer polyvinylpyrrolidone (PVP), yielding supposedly alloy nanoparticles with random atom distribution, or through so-called hydrogen-sacrificial technique, in which nickel hydride, formed by hydrogenation of preformed nickel nanoparticles, reduces and positions Ir atoms in the nanoparticle shell, creating supposedly "Ni core–Ir shell" bimetallic particles (Ni(c) Ir(s), Scheme 1). As demonstrated herein by a variety of



Scheme 1. Formation of Ni(c)Ir(s) nanoparticles by hydrogen-sacrificial method.

characterisation techniques, after the high-temperature polymer removal, the particles either retain or change their initial size depending on the Ni/Ir ratio, and the supposedly coreshell sample exhibits the expected nanoparticle shell enrichment with Ir atoms. Indane RO was studied at atmospheric pressure and 350 °C (Scheme 2). The RO products, if the ring was cleaved only once, were 2-ethyltoluene and *n*-propylbenzene.

Herein, we did not focus on selectivity improvement or cetane number increase, but on a material that will spare rare



Scheme 2. Reaction scheme for ring opening of indane at atmospheric pressure and 350 °C.

and expensive Ir, increase its activity per metal loading in the reactor, and bring no loss to the RO product yield. We only targeted the metal function of the material. We found that the addition of Ni in the core position almost doubled RO activity with the same amount of active Ir in the reactor.

### **Results and Discussion**

#### Characterisation of as-synthesised nanoparticles

The synthesised Ni, Ir and Ni–Ir nanoparticles were analysed by UV/Vis spectroscopy and TEM. In Figure 1, the UV/Vis spectra



Figure 1. UV/Vis spectra taken during the preparation of Ni1Ir1 colloidal dispersion.

taken during the synthesis of Ni1Ir1 colloidal dispersion are shown as an example. No peak was discernible in the UV/Vis range for PVP or ethylene glycol at room temperature. If metallic precursors were added to the solution, peaks appeared at approximately 443 and 496 nm, which can be ascribed to the ligand-to-metal charge-transfer absorption of metallic ions.<sup>[38]</sup> As soon as the NaBH<sub>4</sub> was added, the mixture turned dark brown, a sign of nanoparticle formation. The UV/Vis spectrum collected after heating to reflux confirmed that precursor peaks disappear and absorption increases in the visible region. Metallic nanoparticles absorb photons in UV/Vis region as a result of the coherent oscillation of their conduction band electrons.<sup>[39]</sup>

In Figure 2, size distribution histograms and an exemplary TEM image of the supposedly Ni(c) Ir(s) nanoparticles are presented (other TEM pictures are shown in Figure S1 in the Supporting Information). Particles are nearly spherical with a narrow size distribution. The particles of the Ni(c) Ir(s) sample have the largest size amongst all the synthesised nanoparticles  $(3.2 \pm 0.6 \text{ nm})$ , which implies the hydrogen-sacrificial technique successfully deposited Ir atoms on preformed core Ni particles ( $2.7 \pm 0.7 \text{ nm}$ ). The technique, as shown in Scheme 1, provides the colloidal Ni core particles with hydrogen, which forms Ni–H.<sup>[40]</sup> The hydride species then catalyse the reduction of iridium ions on the surface of Ni core particles, forming coreshell particles. We have recently used this technique to synthesise Pd(c) Ir(s) particles.<sup>[30]</sup>

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**Figure 2.** Size distribution histograms and an exemplary TEM image: a) Ni(c) Ir(s), b) Ni, c) Ni2 Ir1, d) Ni1 Ir1 and e) Ir.  $\sigma$  = Standard deviation

#### Bimetallic interactions in the supported catalysts

The synthetic procedures for bimetallic nanoparticles may form monometallic Ir and Ni nanoparticles, if the final bimetallic system mixes Ni and Ir catalysts, as well as intrinsic bimetallic Ni–Ir nanoparticles. The bimetallic interactions were probed with H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>–TPR) and CO<sub>2</sub> temperature-programmed desorption (CO<sub>2</sub>–TPD) techniques, X-ray photoelectron spectroscopy (XPS) and angle-resolved XPS, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of adsorbed CO and sintering studies. As shown below, the catalytic performance indicates the formation of intrinsic bimetallic nanoparticles as well. For all the analyses, samples were used as in the catalytic experiments, that is, calcined and reduced at 400 °C (apart from TPR).

In Figure 3,  $H_2$ -TPR profiles of selected samples are shown along with deconvoluted peaks for each graph. There are three peaks in the TPR profile of monometallic Ir at 120, 200 and 272 °C, respectively, after deconvolution. The peak at 120 °C may represent the reduction of highly dispersed surface Ir species, which agrees with other results.<sup>[6]</sup> The major peak at 200 °C indicates the reduction of IrO<sub>2</sub>, which is formed during the calcination period before the TPR,<sup>[41,42]</sup> whereas the peak centred at 272 °C resembles documented results for Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>



Figure 3. H<sub>2</sub>–TPR profiles of the selected  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported catalysts. A positive inverted thermal conductivity detector (TCD) signal indicates hydrogen consumption in the H<sub>2</sub>/Ar mixture.

calcined at 420 °C, attributed to the reduction of O-rich complexes.<sup>[41]</sup> The TPR spectrum of Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> reveals a major peak at 219 °C (reduction of NiO phase),<sup>[43]</sup> followed by two smaller peaks at 258 and 316 °C. The latter peaks may show Ni species interacting with the support or the reduction of bulk Ni, because Ni sinters upon calcination as shown below, or both.<sup>[13]</sup>

The deconvolution of bimetallic catalysts' TPR profiles was initiated by assuming the same reduction temperatures as in monometallic samples; a fit could indicate the absence of bimetallic interactions. The TPR profile of Ni1Ir1 reveals three peaks at 150, 210 and 275 °C. The first two peaks appeared at higher temperatures than those of mono-Ir, and the second peak at 210°C can be also ascribed to the contribution from the shifted 219°C Ni peak. This result agrees with the TPR studies of Ir–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, in which intimate contact between the oxide species of Ni and Ir delayed reduction of Ir and facilitated that of Ni.<sup>[13]</sup> Such behaviour is a typical indication of alloy formation, which confirms our hypothesis of intrinsic bimetallic nanoparticle formation instead of the physical mixture of mono-Ir and mono-Ni nanoparticles.<sup>[44]</sup> However, the high-temperature reduction peak centred at 275 °C remained intact, which implies the presence of some segregated mono-Ir oxygen-rich complexes as well.

The deconvoluted TPR spectrum of Ni(c) Ir(s) reveals peaks at 165, 234, 275 and 305 °C. The first two are at higher temperatures than those of the monoforms and indicate bimetallic formation. The peak at 275 °C may indicate either some monometallic Ir particles or the close contact between the Ir atoms in the nanoparticle shell, resembling a monometallic Ir nanoparticle's surface. In addition to the formation of bimetallic species discussed analogously for Ni1 Ir1, the peak at 305 °C may indicate reduction of core Ni atoms in little or no contact with Ir atoms. Thus, TPR profiles reveal bimetallic interactions in the Ni–Ir samples, mostly indicating their intrinsic bimetallic nature, with the possible coexistence of some monometallic Ir structures. Simultaneous reduction for the alloy structure and hydrogen-sacrificial technique for the core–shell does result in different structures, despite the same molar ratio of Ni and Ir.

As Ni and Ir have different chemisorption behaviours toward  $CO_2$ ,<sup>[45]</sup> carbon dioxide was used as a probe molecule on the catalyst surface. In Figure 4 the  $CO_2$ -TPD profiles of selected



Figure 4. CO<sub>2</sub>-TPD profiles of selected  $\gamma$ -Al\_2O\_3 supported catalysts, after subtraction of the TPD data for the support.

supported catalysts are shown after subtracting the reference TPD data for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to eliminate the support effect. A relatively sharp peak is observed for monometallic Ni catalyst at 80 °C, which agrees with the literature, relating to the weakly adsorbed CO<sub>2</sub>.<sup>[46,47]</sup> The Ir catalyst also exhibits a peak at 90 °C but with a more pronounced tail than the Ni catalyst, which continues up to approximately 300 °C. Such tails indicate continuous desorption or dissociation of CO<sub>2</sub> during TPD analysis.<sup>[46]</sup> The core–shell structure's desorption profile can neither prove nor reject bimetallic interactions in the Ni(c) Ir(s) sample, because it may be governed by tightly packed Ir atoms in the nanoparticle shell. However, the Ni1Ir1 sample's peak significantly differs from that of the monoforms, which does indicate bimetallic interactions.

In Figure 5, DRIFT spectra of the adsorbed CO for the same catalysts at frequencies from 1800 to 2150 cm<sup>-1</sup> along with deconvoluted peaks are shown. Deconvolution for bimetallic samples was performed in the same way as for TPR. For monometallic Ir, peaks at 2069, 2008 cm<sup>-1</sup> and 1865 cm<sup>-1</sup> were detected, which agrees with results reported for Ir catalysts.<sup>[48]</sup> The band at 1865 cm<sup>-1</sup> relates to the bridged type of adsorbed CO,<sup>[49]</sup> and the one at 2008 cm<sup>-1</sup> relates to linearly bonded CO.<sup>[50,51]</sup> The band at 2069 cm<sup>-1</sup> may reflect CO molecules adsorbed linearly on large iridium crystallites,<sup>[51]</sup> or Ir-dicarbonyl



Figure 5. DRIFT spectra of the adsorbed CO.

species, in which one Ir atom can accommodate two CO molecules.<sup>[50]</sup> Monometallic Ni catalyst exhibits five peaks from 1824 to 2108 cm<sup>-1</sup>. The 1824 cm<sup>-1</sup> and 1872 cm<sup>-1</sup> bands may reflect the bridged type of adsorbed CO;<sup>[49]</sup> the peaks at 1994 cm<sup>-1</sup> and 2030 cm<sup>-1</sup> the CO molecules adsorbed linearly on Ni particles.<sup>[52]</sup> The two peaks for each adsorption mode may be explained by CO adsorption on metal atoms with different coordination numbers on a nanoparticle surface (terrace, edge and corner atoms).<sup>[49]</sup> The weak band at 2108 cm<sup>-1</sup> may reflect CO adsorption on some Ni<sup> $\delta$ +</sup> species resistant to reduction.<sup>[53]</sup>

In the DRIFT spectra of the two bimetallic samples, the band at 1869 cm<sup>-1</sup> in both Ni1 Ir1 and Ni(c) Ir(s) is positioned between those of mono-Ir and mono-Ni (1865 and 1870 cm<sup>-1</sup>, respectively), which can be related to the bridged adsorbed CO molecules. However, neither sample gives any sign of the 1824 cm<sup>-1</sup> peak of mono-Ni, but both present peaks at positions very close to that of the mono-Ir, which indicates Ir on the samples' surfaces. The bands of 2005 cm<sup>-1</sup> in Ni1Ir1 and 2001 cm<sup>-1</sup> in Ni(c) lr(s) are close to the corresponding peak of the mono-Ir (2008 cm<sup>-1</sup>). The small differences observed can be related to the bimetallic interactions. All three, that is, Ir, Ni1 Ir1 and Ni(c) Ir(s), exhibit a peak at 2069 cm<sup>-1</sup>. Both bimetallic samples also exhibit a peak at 2040 cm<sup>-1</sup>, with higher intensity in Ni1 Ir1 than in Ni(c) Ir(s). The 10 cm<sup>-1</sup> difference with monometallic Ni indicates changes in electronic properties of Ni atoms in the bimetallic samples,<sup>[48, 54, 55]</sup> or new sites created upon alloying.<sup>[54]</sup> Thus, like the TPR results, the DRIFT spectra confirm bimetallic interactions in Ni-Ir samples, with possible coexistence of monometallic Ir clusters.

In Table 1, the XPS binding energy (BE) values of the Ni $2p_{3/2}$  and Ir $4f_{7/2}$  electrons are presented after deconvolution into metallic and oxide components. The BE values of 852.4 and 855.2 eV in Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 60.7 and 62.0 eV in Ir/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> match reported numbers for metallic and oxide Ni and Ir, respective-

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Table 1. XPS binding energy values for Ni and Ir (after peak deconvolution into metallic and oxide components).					
Catalyst <sup>[a]</sup>		Binding en	ergy [eV]	ıy [eV]	
	Ni 2p <sub>3/2</sub>		Ir4f <sub>7/2</sub>		
Ni	852.4	855.2			
Ni2 lr1	852.6	855.6	60.4	61.5	
Ni1 lr1	852.7	855.4	60.7	61.8	
Ni(c) lr(s)	852.6	855.4	60.6	61.9	
lr			60.7	62.0	
[a] Support: γ-/	Al <sub>2</sub> O <sub>3</sub> .				

ly.<sup>[56,57,58]</sup> Bimetallic samples reveal minor but consistent shifts of BE values from those of their monometallic counterparts, approximately 0.2–0.3 eV higher than the BE values of Ni and 0.3 eV lower than from the BE values of Ir implying charge transfer from Ni to Ir upon alloying, which can strengthen the growing evidence of bimetallicity and new clusters. A similar transfer of charge from Ni to Pt upon alloying has been reported in the literature.<sup>[59]</sup>

Angle-resolved XPS (normal, 45° and 60° tilt) was also performed on Ni(c) Ir(s). The normal beam provides the information on the top 8–10 nm of the sample, and the tilted ones reduce the depth by cos45° or cos60° factor (5.6–4 nm). As some Ni(c) Ir(s) particles are close to the 4 nm range (3.2 $\pm$  0.6 nm), we only expected some degree of Ir/Ni intensity ratio increase upon tilting. Indeed, the ratio increased from 0.9 to 1.4, indicating Ir excess on the catalyst surface.

Alloying two metals may increase their resistance to sintering<sup>[41]</sup> as we evaluated as further evidence of bimetallicity. All catalysts were calcined at 400 °C, after depositing them on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, to remove PVP. Monometallic Ni and Ir exhibited different resistance. In Figure 6 and Figure S2, TEM images of fresh and calcined catalysts are shown, and in Table 2 size changes are listed. Monometallic Ni sintered severely after calcination (into agglomerates of approximately 50 nm), whereas mono-Ir retained its size. Oxidative agglomeration of Ir is known to occur at calcination temperatures above 400 °C.<sup>[41,60]</sup> The samples with the Ir-to-Ni molar ratio of equal or larger than 1, in-

Table 2. Size change and the stabiliser removal from the catalysts after calcination. <sup>[a]</sup>					
Catalyst <sup>[b]</sup>	<sup>1)</sup> Nanoparticle size [nm] Before <sup>[c]</sup> After calcination <sup>[d]</sup>		Carbon content <sup>[e]</sup> [wt %]	Carbon rejection after calcination <sup>[f]</sup> [%]	
Ni	2.7±0.7	sintered (up to 50 nm)	8.40	97.4	
Ni2 lr1	$2.5\pm0.5$	agglomerates (up to 10 nm)	-	-	
Ni1 lr1	$2.3\pm0.5$	no change	7.01	99.6	
Ni1 lr3	$2.2\pm0.4$	no change	-	-	
Ni(c) lr(s)	$3.2\pm0.6$	no change	3.99	99.7	
lr	$2.0\pm0.2$	no change	6.90	99.7	

[a] Calcination conditions: T = 400 °C, t = 2 h, in air; [b] Support:  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; [c] Unsupported nanoparticles, based on TEM analysis; [d] Based on TEM analysis, see also Figure 6; [e] Fresh catalyst; [f] Carbon content of pure calcined Al<sub>2</sub>O<sub>3</sub> (0.08 wt%) was subtracted from the numbers reported.

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Figure 6. TEM images of the a, c, e) fresh and b, d, f) calcined (2 h, 400  $^{\circ}$ C) supported catalysts: a, b) Ni; c, d) Ni(c) Ir(s); e, f) Ir.

cluding the core-shell structure, did not sinter. This implies that no monometallic Ni is present in the samples, and supports bimetallicity.

There is no evidence that the synthesised nanoparticles preserved their structure after the high-temperature oxidation and

reduction. On the contrary, particles with low Ir content sintered on calcination, and calcination probably enriched the surface of all Ni-containing nanoparticles with Ni. As the heat of sublimation of Ni  $(101 \text{ kcal mol}^{-1})^{[61]}$  is lower than that of Ir (160 kcal mol<sup>-1</sup>),<sup>[62]</sup> the migration of Ni to the surface would decrease the nanoparticles' surface energy. Both Ni and Ir have the face-centered cubic (fcc) crystal structure and are completely miscible in each other below 1455 °C.<sup>[63]</sup> Within the calcination-reduction temperature range used, we did not expect the bimetallic nanoparticles to transform to a single thermodynamically stable structure, which had previously been shown to occur at approximately 700-800 K for Au-Pt nanoparticles.<sup>[64]</sup> A study of the Pd–Pt nanoparticles' thermodynamic stability revealed that the transformation process becomes significant at approxi-

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mately 1600 K.<sup>[65]</sup> The melting point of NiO is even higher than that of Ni (1960 °C vs. 1455 °C, respectively); thus, the  $O_2$  atmosphere is not expected to promote sintering of the nanoparticles.

The following catalytic reactions were performed at 350 °C after 400 °C calcination and 359 °C reduction. The characterisation analyses described above were conducted after calcination and reduction at 400 °C (higher than the reaction temperature); thus, the results cover the worst-case scenario of bimetallic particle rearrangement owing to hot-spot formation during the reaction. The surface characteristics described can be assumed to be close to the in situ surface arrangement of Ni and Ir.

#### Stabiliser removal before catalysis

The supported catalysts were calcined at 400 °C in air for 2 h before the catalytic reaction to remove PVP. PVP can be adsorbed on the metal surface as a result of hydrophobic interactions,<sup>[66]</sup> thus blocking part of the active surface sites. We did not aim to find the best calcination conditions, but chose a temperature higher than the free PVP decomposition temperature, that is, approximately 350 °C,<sup>[67]</sup> to ensure PVP's removal from particles capable of carbide formation. In Table 2, the carbon content of the selected fresh and calcined catalysts are presented analysed by CHN analysis. The calcination treatment led to more than 99.6% removal of carbon in Ir-containing catalysts (97.4% for Ni), and XPS results revealed no detectable CI or N traces in the samples. This confirms that calcination-reduction successfully rejected PVP and chlorine species.

#### Catalytic activity in indane RO

In Table 3 the catalytic activity results of the synthesised catalysts are shown. As monometallic Ni has no activity for the RO, the results are reported per mole of Ir, and the amount of Ir was standardised (0.8 mg). The negligible Ni RO activity observed is in-line with data presented in the literature: in an extensive study dealing with the RO of several five and six-membered-ring naphthenes,<sup>[1]</sup> the activity of Ir/Al<sub>2</sub>O<sub>3</sub> for the RO of methylcyclopentane at 275 °C was found to be 50 times higher than that of the Ni/Al<sub>2</sub>O<sub>3</sub>.

Table 3. C ne. <sup>[a]</sup>	atalytic activit	y of the syntl	esised catalysts in atmospheric RO of inda-	
Catalyst <sup>[b]</sup>	Ni/Ir loa- ding [wt%]	Activity [10 <sup>-1</sup> mol <sub>inda</sub>	$\underset{ne}{\text{mol}_{Ir}^{-1}\text{min}^{-1}} [10^{-1}\text{mol}_{(\text{ET}+\text{PB})}\text{mol}_{Ir}^{-1}\text{min}^{-1}\text{c]}$	
Ni	0.165/0	< 0.1	< 0.1	
Ni2 lr1	0.067/0.118	1.3	1.2	
Ni1 lr1	0.044/0.163	5.6	4.5	
Ni1 lr3	0.022/0.218	5.1	3.9	
Ni(c) lr(s)	0.052/0.165	8.3	6.4	
lr	0/0.220	4.3	3.4	
[a] Reaction conditions: $T=336$ °C, 125 min on stream; samples with 0.8 mg of Ir were used for each activity measurement. [b] Support: $\gamma$ -Al <sub>2</sub> O <sub>3</sub> . [c] ET=2-ethylto-luene, PB= <i>n</i> -propylbenzene.				

The addition of Ni to Ir with a molar ratio of equal or less than 1 increased the catalytic activity. Above the specified ratio, the activity dropped significantly as shown for Ni2Ir1. However, the highest Ir-to-Ni ratio of 3 and the absence of Ni did not lead to the highest activity. That was observed for the 1/1 Ni(c) Ir(s) sample, which had almost twice the activity of monometallic Ir, and 50% more than the Ni1Ir1 sample with the same metal ratio but synthesised by simultaneous metal reduction. Thus, the hydrogen-sacrificial technique is paramount for achieving the highest activity. Since the amount of Ir used was the same, and monometallic Ir does not sinter, the observed activities further confirm bimetallicity, although the presence of some monometallic Ir nanoparticles cannot be excluded.

An interesting coincidence was found if calculating the turnover frequency (TOF) for the monometallic Ir catalyst. Based on the diameter of an Ir nanoparticle (2.0 nm) and assuming an ideal fcc cuboctahedron crystal with a unit-cell parameter of 0.384 nm, we found Ir dispersion based on van Hardeveld and Hartog's surface statics as 61%,<sup>[68]</sup> yielding TOFs of 0.7 mo- $I_{indane}$  mol<sub>surface Ir</sub><sup>-1></sup> min<sup>-1</sup>. This value is almost the same as the activity value of 0.8 mol<sub>indane</sub> mol<sub>Ir</sub><sup>-1</sup> min<sup>-1</sup> for the Ni(c)Ir(s) catalyst. The similarity indicates that in the latter catalyst all Ir atoms are accessible to the reactant, meaning they are in the nanoparticle shell, with Ni supporting them. However, synergism cannot be excluded, because some monometallic Ir nanoparticles with lower dispersion may be also present.

The core-shell sample also allowed the highest production rate of single-cleavage products (i.e., 2-ethyltoluene and *n*-propylbenzene). The lower selectivities of this catalyst for 2-ethyltoluene and *n*-propylbenzene than those of the other catalysts (see Table 4) should not be used for comparison, because they were observed at much higher conversions. Ni addition did not improve the ratio of *n*-propylbenzene to 2-ethyltoluene. This is in-line with the dicarbene RO mechanism, which results in the cleavage of unsubstituted secondary-secondary carbon atom bonds, i.e., yielding 2-ethyltoluene for this specific reaction, and agrees with the literature, which suggests a dicarbene mechanism domination for both Ni and Ir in RO reactions.<sup>[1,7]</sup> As a result of this work, we can replace the rare and expensive Ir

with Ni and increase the RO activity per total Ir loading in the reactor.

The results obtained can be compared with reported data on the atmospheric RO of indane at 325 °C using a series of in-house Pt–Ir catalysts.<sup>[7,44,48]</sup> For the most active bimetallic formulation of Pt5Ir95 (based on wt%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the product selectivities at 55% indane conversion at 275 min on stream were reported as 67.1, 8.8, 12.9, 3.1, 4.1, 0.4 and 3.6 (wt%) for 2-ethyltoluene, *n*-propylbenzene, *o*-xylene, ethylbenzene, toluene, benzene and lights, respectively.<sup>[7]</sup> These selectivities match the selectivities of our Ni1Ir3 catalyst (or Ni9Ir91 in wt%), as demonstrated in Table 4. This finding indicates that Pt can be successfully replaced by Ni without loss in selectivity. In terms of activity, using the reported

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Catalyst <sup>[b]</sup>	Selectivity [wt%]						
	2-Ethyltoluene	n-Propylbenzene	<i>o</i> -Xylene	Ethylbenzene	Toluene	Benzene	Light hydrocarbons
Ni <1% conversion							
Ni2 lr1	69	20	3	0	4	2	2
Ni1 lr1	64	17	10	1	4	1	3
Ni1 lr3	66	11	13	2	5	0	3
Ni(c) Ir(s)	51	9	20	3	9	1	7
lr	64	16	10	1	4	1	4

values for Pt5 Ir95 catalyst (H<sub>2</sub> flow 4.8 dm<sup>3</sup>(n) h<sup>-1</sup>, H<sub>2</sub>/indane molar ratio of 63, catalyst amount 0.3 g, sum of metal loadings 2 wt% <sup>[44]</sup> and 83% dispersion<sup>[48]</sup>) the TOF can be calculated as 1.2 mol<sub>indane</sub> mol<sub>surface atoms</sub><sup>-1</sup>min<sup>-1</sup>. The TOF value for our Ni(c) Ir(s) catalyst at the same 325 °C can be estimated from 0.8 mol<sub>indane</sub> mol<sub>surface atoms</sub><sup>-1</sup>min<sup>-1</sup> at 336 °C and the reaction activation energy of 78 kJ mol<sup>-1</sup> (found previously for the monometallic Ir catalyst<sup>[69]</sup>) as 0.6 mol<sub>indane</sub> mol<sub>surface atoms</sub><sup>-1</sup>min<sup>-1</sup>. Considering the fact that the data stem from two different groups, the value may be considered comparable to the value for the Pt5 Ir95 catalyst; however, the catalyst reported herein does not contain Pt and has a lower amount of Ir.

The TEM picture of exemplary Ni1Ir1 catalyst before and after the catalytic reaction (200 min) is presented in Figure 7 and reveals no observable particle sintering after the reaction.



Figure 7. TEM images of Ni1 Ir1 catalyst: a) before the catalytic reaction (calcined and reduced in situ) and b) after the 200 min on stream.

### Conclusion

The correct method to synthesise bimetallic nanoparticles is essential in developing a material with enhanced catalytic performance. A 1:1 molar ratio of Ni/Ir led to doubled catalytic activity only if Ir was placed preferably in the nanoparticle shell. This was possible owing to applying a hydrogen-sacrificial technique applied to preformed Ni core nanoparticles, as opposed to the simultaneous reduction of Ni and Ir precursors. Transmission electron microscopy, X-ray photoelectron spec-

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troscopy, CO diffuse reflectance infrared Fourier transform spectroscopy, temperature-programmed reduction and CO<sub>2</sub> temperature programmed desorption and CHN analysis were performed on a variety of Ni-Ir nanoparticles synthesised in the presence of polyvinylpyrrolidone and deposited on alumina followed by high-temperature polymer removal. The particles were mostly bimetallic, and the presence of Ir enhanced their

stability towards sintering. The Ni(core)–Ir(shell) catalyst exhibited twice higher activity in indane ring opening at 350 °C than monometallic Ir, and allowed higher yield of single cleavage products. Ni presence did not change the dicarbene path for ring-opening characteristic of Ir. The study has developed a material that will spare rare and expensive iridium and enhance its performance. Supposedly, the introduction of acidic function into the support may further improve ring opening yield by the 6-member ring isomerisation to a 5-member ring.

### **Experimental Section**

### Materials

Hydrogen hexachloroiridate(IV) hydrate (H<sub>2</sub>Cl<sub>6</sub>Ir·x H<sub>2</sub>O, Sigma–Aldrich), nickel chloride hexahydrate (NiCl<sub>2</sub>·6 H<sub>2</sub>O, Sigma–Aldrich), polyvinylpyrrolidone (PVP, average molecular weight 40 000, Sigma–Aldrich), sodium borohydride (NaBH<sub>4</sub>, Sigma–Aldrich), gamma alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, average pore size 58 Å, specific surface area 155 m<sup>2</sup>g<sup>-1</sup>, Sigma–Aldrich), ethylene glycol (Fischer Scientific) and acetone (> 99.7 %, Fischer Scientific) were used as received. Nitrogen, argon and hydrogen of ultrahigh purity (99.999%) were purchased from Praxair. Benzocyclopentane (indane, 95 vol%, Sigma–Aldrich) was distilled once.

### **Catalyst preparation**

Ni and Ir mono- and bimetallic nanoparticles were preformed in a colloidal dispersion before deposition on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. A modified polyol process, which applies a strong reducing agent, NaBH<sub>4</sub>, was adapted for the synthesis of nanoparticles in this study. The method has precedent for Ni.<sup>[70]</sup> Quantities of 0.1 mmol of either Ni or Ir metal precursor were dissolved in 25 mL of ethylene glycol and added to a 500 mL three-neck flask. PVP was then added with the PVP/metal ratio of 40:1 and 20:1 (molar basis) to the Ni and Ir containing flasks, respectively. The final volume of the solution was increased to 175 mL by adding extra ethylene glycol. The resulting mixture was stirred vigorously under a constant flow of nitrogen and heated until the temperature reached 130-140 °C. NaBH<sub>4</sub>  $(\approx 0.38 \text{ g})$  was added to the flask at this temperature very quickly with adequate care. The reduction reaction occurred immediately, the solution turned into dark brown with vapour release. Heating was continued until the mixture came to boil at approximately 197°C and then heated at reflux in air for 1 h to complete the synthesis of PVP-protected nanoparticles. No precipitate was observed at the end of synthesis.

Bimetallic nanoparticles were synthesised with either simultaneous reduction of metal precursors (co-reduction) or the successive reduction assisted by hydrogen (hydrogen-sacrificial reduction method) to produce random alloy and core-shell particles, respectively. The PVP/(Ir+Ni) ratio of 20:1 (molar basis) was used for all the bimetallic nanoparticles. Three different Ni-Ir alloys with the molar ratios of Ni/Ir=3:1, Ni/Ir=1:1 and Ni/Ir=1:3 were synthesised by the co-reduction of the metallic precursors. In all cases, quantities of 0.1 mmol of (Ni+Ir) were used and the same amount of NaBH<sub>4</sub> (0.38 g) was added at 130-140 °C. The resulting colloidal solution obtained was always macroscopically homogeneous and transparent without any precipitate. As the final Ni/Ir molar ratios in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported catalysts were found as 1.9:1, 0.9:1 and 1:3, respectively, they are referred as Ni2Ir1, Ni1Ir1 and Ni1Ir3. In addition to the alloy particles mentioned above, another bimetallic nanoparticle composition, Ni(core)-Ir(shell) was synthesised (with the molar ratio of 1:1) using the hydrogen-sacrificial reduction method, and referred as Ni(c) Ir(s). For the latter combination, Ni core nanoparticles were synthesised as detailed below. After the heating time at reflux, colloidal solution was allowed to cool to RT followed by purging with hydrogen for 1.5 h. This procedure creates Ni hydride,<sup>[40]</sup> which further served to reduce Ir and forms an Ir shell around the preformed Ni nanoparticles. To build an Ir shell,  $H_2Cl_c Ir \cdot x H_2O$  (0.1 mmol) was dissolved in ethylene glycol ( $\approx$  50 mL) and added to the mixture of Ni nanoparticles drop by drop. A syringe pump (Fisher Scientific 01001) was used to transfer Ir solution to the synthesis flask with a flow rate of approximately  $20 \mbox{ mL} \mbox{ h}^{-1}.$  The synthesis flask was constantly purged with  $\mbox{ H}_2$ during the addition of Ir and at least one hour afterwards. Each resulting colloidal dispersion was macroscopically homogeneous and transparent with no precipitate.

All synthesised nanoparticles were supported on pre-dried  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by using acetone to precipitate them.<sup>[71]</sup> Acetone ( $\approx$  800 mL) was added to the suspension of nanoparticles (in colloidal solution) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and it was stirred vigorously for 2 h. Then, the supernatant was removed from the beaker and the resulting powder was washed several times with acetone and dried at ambient overnight to form fresh catalysts, which then were calcined in air at 400 °C for 2 h to ensure PVP removal.

### **Catalyst characterisation**

Formation of nanoparticles in the colloidal solution was studied by UV/Vis spectroscopy by using a Varian Cary 50 Scan UV visible spectrometer with a 1 cm quartz cell.

TEM images of as-synthesised and supported nanoparticles were recorded with a JEOL JEM 2100 TEM device with a LaB6 filament operating at 200 kV. The system was equipped with a Gatan GIF Tridiem energy filter with a  $2k \times 2k$  digital camera. Samples for TEM analysis were prepared by placing a drop of the colloidal dispersion of nanoparticles onto a carbon-coated copper grid, followed by the evaporation of the solvent in a vacuum oven at 50 °C. The average diameter and the standard deviation were calculated by counting over 200 particles by using the ImageJ software. In the case of supported catalysts, the sample (0.1 g) was suspended in ethanol (5 mL) and dispersed in an ultrasonic bath for approximately 5 min before placing a drop of the suspension on the TEM grid.

The loading of the Ni and Ir in the calcined catalysts was determined by neutron activation analysis at the University of Alberta SLOWPOKE facility. Samples were irradiated in the nuclear reactor for 600 s following a decay period of  $\geq$  24 h. Irradiated samples were individually counted for 600 s using a 22% relative efficiency ORTEC hyperpure Ge detector housed in a 10 cm Pb cave. The Ge detector was connected to a PC-based Aptec multichannel analyser card.

Fresh and calcined supported catalysts were analysed by an Elementar Vario Micro elemental analyser for CHN percentage.

H<sub>2</sub>-TPR was performed by using an AutoChem 2950 HP device (Micromeritics). Quantities of approximately 500 mg of the calcined catalysts were used for the analysis. Samples were initially reduced in a 50 mL min<sup>-1</sup> flow of a mixture of 10% H<sub>2</sub> in Ar at T=400 °C for 1 h, then cooled to ambient temperature and oxidised in a 50 mL min<sup>-1</sup> flow of 10% O<sub>2</sub> in He at T=400 °C for 1 h. The TPR profiles were collected with a 10 mL min<sup>-1</sup> mixture of 10% H<sub>2</sub> in Ar from ambient temperature to 400 °C with a heating rate of 10 °C min<sup>-1</sup>. Peak deconvolution was performed by using Origin software.

CO<sub>2</sub>−TPD was performed with the same AutoChem 2950 HP device. Quantities of approximately 250 mg of the similar calcined catalysts but with higher metal loading (≈ 1 wt%) were used for this study because the Al<sub>2</sub>O<sub>3</sub> also adsorbed CO<sub>2</sub>. Before CO<sub>2</sub> adsorption, samples were initially outgassed in Ar at 300 °C for 2 h, and then reduced by a mixture of 10% H<sub>2</sub> in Ar at 400 °C for 1 h. After the reduction pretreatment, the active gas was switched to He and the temperature was reduced to 50 °C. A mixture of 3% CO<sub>2</sub> in He was passed through the samples at 50 °C for 1 h with the flow of 50 mLmin<sup>-1</sup>. Physically adsorbed CO<sub>2</sub> was then removed by flushing 50 mLmin<sup>-1</sup> of He at 50 °C for 1 h. The TPD spectra were collected by flowing 20 mLmin<sup>-1</sup>.

DRIFTS of adsorbed CO was performed with a Nicolet Nexus670 spectrophotometer, at a resolution of 4 cm<sup>-1</sup>in the range 800-3000 cm<sup>-1</sup>and averaged over 128 scans. The Ni–Ir nanoparticles were supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with the higher loading of approximately 1 wt %. Following the same calcination treatment, that is, 2 h at 400 °C in air, catalysts were reduced in the AutoChem 2950 with a flow of 50 mL min<sup>-1</sup> of 10% H<sub>2</sub> in Ar from ambient temperature to 400 °C and kept for 1 h. Subsequently, they were allowed to cool to RT under a flow of Ar and later a mixture of 3% CO in He with a flow of 50 mLmin<sup>-1</sup> was passed over the samples for approximately 45 min. CO-adsorbed catalysts were further treated with a flow of Ar at RT for approximately 30 min to desorb the physically adsorbed CO; the DRIFTS spectra of the CO-adsorbed catalysts were recorded immediately. KBr from Sigma-Aldrich was dried at approximately 200°C overnight and used for collecting the background spectra. Samples were also diluted with KBr at the ratio of approximately 20 wt.% before placing in the DRIFTS cell. The reflectance spectra of the catalysts were transformed to Kubelka-Munk using the OMNIC software. OMNIC and Origin software were used for further data processing, visualisation and deconvolution of the spectra.

XPS was performed by using a Kratos Axis 165 X-ray photoelectron spectrometer with a mono Al<sub>Ka</sub> source operating at 15 mA and 14 kV. The XPS analysis was done on pelletised samples that were calcined in air at 400 °C for 2 h followed by the reduction in hydrogen at 400 °C for 1 h. Background subtraction (Shirley-type), smoothing and peak fitting were performed by using the CasaXPS software package. All the core-level spectra were corrected with C 1 s at 284.6 eV.

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#### Catalytic behaviour in indane RO

Catalytic studies were performed at atmospheric pressure in a flow stainless-steel reactor (length 0.406 m, inner diameter 0.013 m). Calcined catalysts were diluted with #150 mesh SiC ( $\approx$  2 g). Catalyst amounts corresponding to 0.8 mg Ir were used for each run except for monometallic Ni, in which 0.8 mg Ni used. Gas flows were regulated with calibrated mass-flow controllers (Sierra Instruments). The system was purged with Ar before and after each test. Catalysts were initially pretreated in situ with 80 mLmin<sup>-1</sup> H<sub>2</sub> from ambient temperature to 359°C for 1 h. Afterwards, the reactor temperature and the H<sub>2</sub> flow rate were changed to 350 °C and 120 mLmin<sup>-1</sup>, respectively. The catalytic reaction started by bubbling hydrogen through the indane bubbler kept at the constant temperature water bath of 10°C that corresponds to 70.8 Pa indane partial pressure assuming saturation. The actual pressure was found as 68.4 Pa and indane flow rate of  $2.8 \times 10^{-5}$  g min<sup>-1</sup> was confirmed with GC, which was calibrated with a Gilson HPLC pump. The reaction products were analysed online every 25 min with a 430 Varian Gas chromatograph equipped with an FID detector; the details has been explained previously.  $\ensuremath{^{[30]}}$  Each catalyst was tested for 200 min on stream and 6 data points were collected at 75, 100, 125, 150, 175 and 200 min. Results were repeatable within 2-5% experimental error. The absence of external and internal mass transfer limitations was verified experimentally by the Madon-Boudart method. Within the indicated times on stream, catalysts did not show significant deactivation. The reaction products were confirmed by an Agilent Technologies 7890 GC coupled with a 5975C MSD as described previously.<sup>[30]</sup>

The desired single-cleavage products of RO were 2-ethyltoluene and *n*-propylbenzene. Main dealkylation products were *o*-xylene, ethylbenzene, toluene and benzene. Compounds with GC retention times less than that of benzene were named "lights". The same main products were reported in ring opening of indane over Pt–Ir catalysts.<sup>[7]</sup>

Selectivity values are reported not on mole, but on a mass basis (because up to nine moles of methane may be produced from one mole of indane). Response factors of different products with respect to indane were found by performing GC flame ionisation detector calibration with reference gas cylinders.

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**Keywords:** alloys · cleavage reactions · iridium · nickel · nanoparticles

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