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Nitrogen-Doped Carbon Encapsulated Nickel/Cobalt Nanoparticle Catalysts for Olefin Migration of Allylarenes

Søren Kramer, Jerrik Mielby, Kasper Buss, Takeshi Kasama, Søren Kegnæs*

Abstract: Olefin migration of allylarenes is typically performed with precious metal-based homogeneous catalysts. In contrast, very limited progress has been made using cheap, earth-abundant base metals as heterogeneous catalysts for these transformations – in spite of the obvious economic and environmental advantages. Herein, we report on the use of an easily prepared heterogeneous catalyst material for the migration of olefins, in particular allylarenes. The catalyst material consists of nickel/cobalt alloy nanoparticles encapsulated in nitrogen-doped carbon shells. The encapsulated nanoparticles are stable in air and easily collected by centrifugation, filtration, or magnetic separation. Furthermore, we demonstrate that the catalysts can be reused several times providing continuously high yields of the olefin migration product.

The 1-propenylarene motif is ubiquitous in Nature. This core structure is found in many naturally occurring compounds that exhibit desirable properties such as antibiotic, anti-inflammatory, anti-fungal, and anti-pesticidal activity (Figure 1).[1] Furthermore, 1-propenylarenes are used as synthetic precursors for more complex targets with pharmacological activities.[2]

One of the most straightforward routes to the high-value 1-propenylarene motif is olefin migration of easily accessible allylarenes.[1,3] While homogeneous systems applying many different metals have been reported for this transformation, catalysts based on precious metals are in general dominating.[4] Replacement of these expensive catalysts with much more abundant base metals such as nickel and cobalt is highly advantageous from an environmental and economic perspective. In recent years, significant advancement of olefin migration using homogeneous nickel and cobalt catalysts have been achieved.[5-7] For sustainable chemical production, heterogeneous catalysts often present several advantages over homogeneous catalysts such as robustness, ease of separation from reaction mixture, and recyclability.[8] However, very limited progress has been made for the corresponding cobalt and nickel heterogeneous systems.[9]

Recently, metals supported on nitrogen-doped carbon have found use as very powerful heterogeneous catalysts in a number of organic reactions, especially for transformations involving catalyzed hydrogenation and/or dehydrogenation steps.[10,11] A strong interaction between metal nanoparticles and the nitrogen-doped carbon support is believed to account for the enhanced stability of these catalyst materials.[12] Still, in some cases, loss of activity is observed under thermal conditions and even more stable catalysts are warranted.[10c] In this regard, the use of encapsulated metal nanoparticles, whereby each nanoparticle is protected by a thin shell of nitrogen-doped carbon support, could be a promising direction to explore.[13]

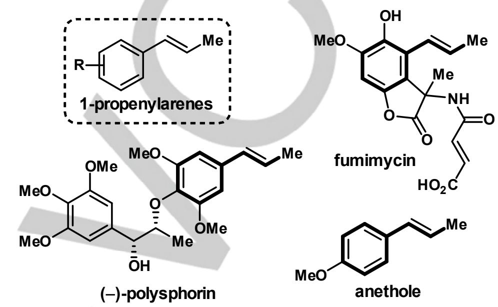

Figure 1. Naturally occurring 1-propenylarenes.[1]

Herein, we report the use of an easily prepared material consisting of nickel/cobalt alloy nanoparticles encapsulated in nitrogen-doped carbon shells as a heterogeneous catalyst for the migration of olefins, in particular allylarenes, to form 1-propenylarenes. The transformation does not involve hydrogenation and/or dehydrogenation steps and the catalyst is robust even under thermal conditions as illustrated by catalyst recycling.

The encapsulated NiCo nanoparticles were prepared based on a method recently reported by Deng *et al*.[13c] In this method, the Ni and Co precursors are dissolved in methanol and precipitated with ethylenediaminetetraacetic acid (EDTA) under autogenous pressure in an autoclave at 200 °C. The precipitated metal-EDTA complex is then collected by filtration and carbonized under an inert atmosphere. In order to investigate the effect of the Ni/Co ratio, we synthesized and characterized a series of encapsulated nanoparticles with varied metal composition. The resulting catalysts are denoted Ni_xCo_y@NC where x and y indicates the molar ratio of Ni/Co and NC is an abbreviation for nitrogen-doped carbon.[14]

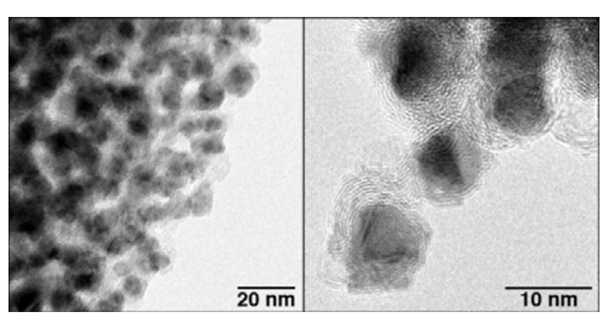

Figure 2. a) BF-TEM image of Ni_1Co_1@NC. b) Magnified image showing graphitic carbon layers covering the nanoparticles.

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Figure 2 shows a representative bright-field transmission electron microscope (BF-TEM) images of the Ni_1Co_1@NC catalyst. The images indicate that the metal nanoparticles were completely covered by several layers of graphitic carbon containing ~1% of nitrogen. Electron diffraction suggests that the phase is a NiCo alloy with a FCC structure.[14] The average size of the encapsulated nanoparticles was around 10 nm as measured from ~250 nanoparticles, which is in good agreement with broad diffraction peaks in X-ray diffraction (XRD).

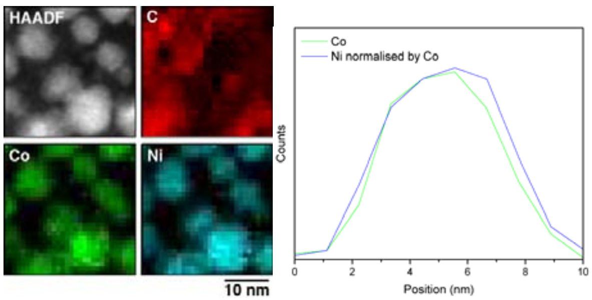
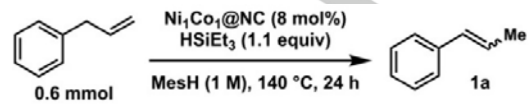


Figure 3. a) HAADF-STEM image along with the elemental distribution of C, Co, and Ni determined by EDX. b) Elemental profiles across a single nanoparticle.

Figure 3a shows a high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) image of the Ni_1Co_1@NC catalyst and the corresponding energy dispersive X-ray (EDX) maps for C, Co, and Ni, respectively. The elemental mapping confirms that Ni and Co were evenly distributed, which is also evident from Figure 3b, showing EDX elemental profiles measured across an individual nanoparticle. EDX and electron energy loss spectroscopy (EELS) show some surface oxidation signals since the specimen was exposed to air prior to analysis. Overall, the various characterizations revealed that the materials were different from those reported by Deng et al. in terms particle size and in particular elemental composition.[14]

With the in-depth characterization of the material in hand, the catalytic features of the material toward olefin migration of allylbenzene was tested. Subjecting allylbenzene to 8 mol% Ni_1Co_1@NC (4 mol% of each metal) in the presence of 1.1 equivalents of $HSiEt_3$ at 140 °C in mesitylene afforded a high yield of 1-propenylbenzene (**1a**) with good *E*-selectivity (Table 1, entry 1). The influence of various reaction parameters on the reaction outcome is shown in Table 1. Minimal conversion takes place in the absence of either catalyst or silane (entries 2 and 3). Decreasing the amount of silane to 0.5 equivalents as well as using more concentrated or diluted reaction media led to incomplete conversion after 24 hours (entries 4–6). In other aromatic solvents than mesitylene, the reaction is less facile (entries 7–9). When the reaction was performed under an air atmosphere, the catalysis was suppressed (entry 10).[15] In all cases, only small amounts (≤5%) of propylbenzene from alkene hydrogenation were detected.

Table 1. Influence of various reaction parameters on reaction efficiency. [a]



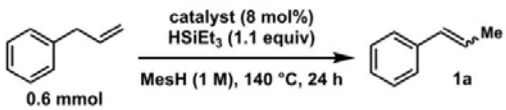
Entry	Change from standard conditions	Yield of **1a** [%][b]	[*E*:*Z*]
1	none	92	84:16
2	no Ni_1Co_1@NC	5	-
3	no $HSiEt_3$	7	-
4	0.5 equiv $HSiEt_3$	70	81:19
5	0.5 M instead of 1.0 M	85	77:23
6	2.0 M instead of 1.0 M	83	85:15
7	PhMe, 100 °C[c]	43	84:16
8	PhOMe[c]	53	87:13
9	PhCN[c]	12	-
10	reaction under air	5	-

[a] All data are the average of two experiments. [b] GC-FID yield with the aid of a calibrated internal standard. [c] 13 mol% Ni_1Co_1@NC used as catalyst.

Next, we examined the influence of the catalyst composition on the conversion and product distribution (Table 2). Materials containing either pure cobalt or predominantly cobalt core nanoparticles were ineffective as catalysts (entries 1 and 2). In contrast, the materials primarily consisting of nickel could catalyze the allylbenzene migration (entries 4 and 5).[16] Interestingly, the material containing equal amounts of both metals displayed a superior yield compared to the other metal compositions (entry 3). That the presence of a nickel/cobalt alloy is crucial for the reaction outcome was further highlighted in a reaction using a mixture of the pure metal materials. Using 4 mol% Ni@NC in combination with 4 mol% Co@NC led to only 45% yield of the styrene product (entry 6). The dependence on the metal core illustrated in Table 2 also indicates that the nitrogen-doped carbon support is not an active catalyst by itself.

When monitoring the reaction progress over time, no induction period was observed and the conversion was linear until approximately 50% conversion.[14] However, an interesting switch in selectivity was detected (Figure 4a). After an initial burst with very high *Z*-selectivity, the following conversion of allylbenzene occurs with apparent excellent *E*-selectivity (~95:5). Initially, we suspected that the selectivity switch could originate from an in-situ modification of the catalyst. However, examining a batch of used catalyst by transmission electron microscopy did not reveal any obvious change in the catalyst.[14] Instead, we investigated the possibility of product isomerization under the reaction conditions (Figure 4b). Subjecting a mixture of allylbenzene and (*Z*)-1-propenylbenzene ((*Z*)-**1a**) to the standard conditions led to a significantly higher yield of (*E*)-1-propenylbenzene than that which could be expected from Figure

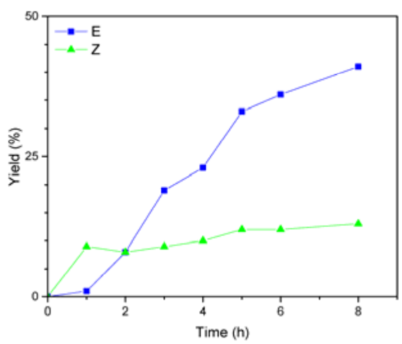
Table 2. Influence of catalyst composition on reaction efficiency. [a]



Entry	Catalyst	Yield of **1a** [%][b]	[*E*:*Z*]
1	Co@NC	9	0:100
2	Ni_1Co_3@NC	9	0:100
3	**Ni_1Co_1@NC**	**92**	**84:16**
4	Ni_3Co_1@NC	76	81:19
5	Ni@NC	56	79:21
6	Co@NC + Ni@NC[c]	45	73:27

[a] All data are the average of two experiments. [b] GC-FID yield with the aid of a calibrated internal standard. [c] 4 mol% of each catalyst.

4a, if no isomerization of (*Z*)-**1a** takes place. Accordingly, this experiment indicates that, for the standard reaction, once the concentration of *Z*-product builds up, the rate of isomerization equals the rate of the olefin migration from allylbenzene forming (*Z*)-1-propenylbenzene.[17,18]



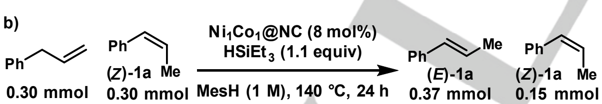
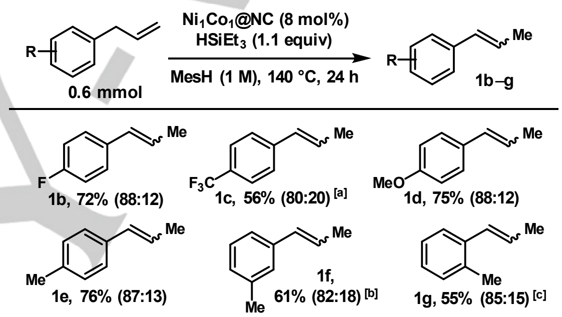


Figure 4. a) *E*/*Z*-Selectivity as a function of reaction time. b) Probing for in-situ isomerization of the product.

Hot filtration of a standard reaction after 5 hours led to a clear colorless filtrate, which was inactive toward olefin migration of allylbenzene. X-ray fluorescence (XRF) of the filtered reaction mixture showed no trace of cobalt and only 0-80 ppm of nickel.[19] Furthermore, the addition of 75 equivalents mercury after 4 hours led to a complete stop of catalytic turnover. In combination, these data strongly support that the active catalyst is heterogeneous and insoluble.[20] Accordingly, catalyst recycling was attempted. Separation of the liquid phase by magnetic filtration followed by addition of a fresh stock solution containing $HSiEt_3$ and allylbenzene afforded continuously high yields and stereoselectivites of **1a**: 1st run: 92% (84:16); 2nd run: 91% (86:14); 3rd run: 91% (87:13); 4th run: 95% (86:14).[21]

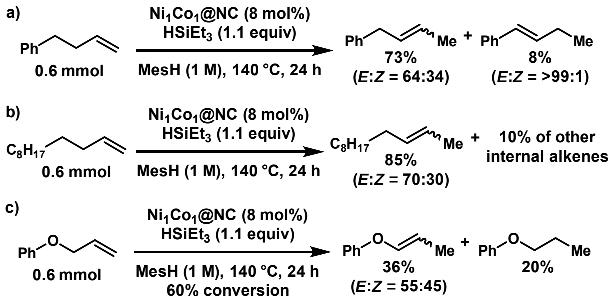
In order to evaluate the generality of the developed reaction, different allylarenes were subjected to the optimized reaction conditions (Scheme 1). Both substrates bearing either electron-withdrawing groups (F and CF_3), or an electron-donating group (OMe) were well tolerated. Encouraged by these results, a series of allyltoluenes were used to examine the influence of steric effects on the reaction outcome. It was found that as the methyl group is moved closer to the allyl moiety, a slight decrease in reactivity is observed. Interestingly, no change in stereoselectivity was observed across this series. In summary from the substrate scope, electronic and steric effects have very limited influence on the stereoselectivity, however, both factors can affect the substrate reactivity. It should be noted that for substrates displaying decreased reactivity, the yields based on conversion were in still high.[22]



Scheme 1. Substrate scope of the developed reaction. All data are the average of two experiments. Yields are based on GC-FID analysis with the aid of a calibrated internal standard. *E*:*Z* ratios are in parenthesis. [a-c] For some substrates incomplete conversion was observed; the yields based on recovered starting material for these substrates are: [a] 84%, [b] 92%, [c] 81%.

In order to expand the substrate scope beyond allylarenes, isomerizations of 4-phenyl-1-butene and 1-dodecene were performed (Scheme 2a and b). In both cases, high conversions to internal olefins were achieved. Interestingly, the reactions displayed good selectivity for one position migration leading to high yields of the corresponding 2-alkenes. The slight decrease in *E*:*Z* selectivity when comparing to allylarenes could indicate that there is a minor influence from steric effects after all.

Olefin migration of allyl phenyl ether, even with poor stereoselectivity, followed by hydrolysis would allow for deprotection of allyl-protected phenols.[23] When subjecting allyl phenyl ether to the standard reaction conditions, the major product was indeed the desired phenyl vinyl ether (Scheme 2c). However, the reaction was only 60% selective for the desired vinyl ether while hydrogenation accounted for the rest of the mass balance.



Scheme 2. Isomerization of a) 4-phenyl-1-butene, b) 1-dodecene, and c) allyl phenyl ether. Yields are based on ^{1}H NMR analysis of the crude reaction mixture relative to an internal standard.

In summary, we have demonstrated that a heterogeneous catalyst, based on the earth-abundant metals nickel and cobalt, can facilitate olefin migration producing highly valuable 1-propenylarenes. The catalyst material, consisting of metal alloy nanoparticles encapsulated in nitrogen-doped carbon, is readily prepared from cheap and commercially available precursors. Furthermore, the heterogeneous nature of the catalysis ensures easy recovery and reuse of the catalyst. For the allylarene substrates, this new heterogeneous system can match the TOF and selectivity of previously reported homogeneous nickel and cobalt catalysts.[5b,7b] In addition to allylarenes, the developed catalytic system can also be applied for the selective one position migration of aliphatic olefins. Finally, preliminary studies on reaction progress and pathway were disclosed.

Acknowledgements

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Keywords: Olefin migration • nanoparticles • N-doped carbon • base metals • catalysis

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[18] Olefin migration/isomerization using homogeneous cobalt catalysis has been proposed to proceed through a radical pathway. Consistent with this hypothesis, our standard reaction was completely suppressed by

the addition of 20 mol% BHT. However, no radicals were observed by EPR of a filtered aliquot of the reaction mixture.

[19] XRF analysis was performed on the filtrate of two separate reactions with identical conversions and yields. In both cases, the cobalt content in the filtrate was below the detection limit (≤1 ppm). For nickel, the first reaction had ≤1 ppm of nickel in the filtrate and the second 80 ppm.

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[21] Only 5-10% of the added $HSiEt_3$ is consumed during a reaction. Interestingly, a recycling experiment without addition of $HSiEt_3$ in the 2nd cycle did not afford any conversion. Accordingly, the role of the silane does not appear to be limited to a possible initial reduction of the catalyst surface. See Supporting Information.

[22] For the reactions in Table 1, Table 2, and Scheme 1, good reproducibility was observed with the yields of duplicate experiments falling within a range of ± 2% of the reported average value.

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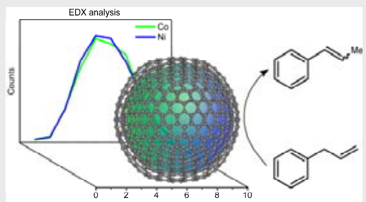
Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

"Het" the base: A heterogeneous base metal catalyst is applied for olefin migration. Specifically, this nickel and cobalt-based nanoparticle catalyst can be used for accessing the ubiquitous 1-propenylarene motif by means of stereoselective olefin migration of easily accessible allylarenes.



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Layout 2:

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