Application of N-doped carbon-encapsulated metal nanoparticles as heterogeneous catalysts in organic reactions

Søren Kramer[a], Jerrik Mielby[a], Søren Kegnæs[a,*]
[a]*Technical University of Denmark, Kgs. Lyngby, 2800, Denmark*
**Corresponding author: skk@kemi.dtu.dk*

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. Further, the catalyst was also applied in silylative pinacol coupling of arylaldehydes. The catalyst material consists of nickel/cobalt alloy nanoparticles.

Keywords: Nanoparticles, nitrogen-doped carbon, mechanism.

1. Introduction

While industrial catalysts are mainly heterogeneous systems, i.e. solid catalysts with reactants in gas- or liquid phase, around 25 % of catalytic processes are homogeneous, i.e. molecular catalysts in the same phase as the reactants. It is especially the processes involving production of bulk organic chemicals and fine chemicals that utilize homogeneous catalysis. Such processes often require a deep mechanistic understanding of the catalytic reaction or a non-polar environment, both of which are easier achieved using homogeneous catalysis. However, for industrial applications, homogeneous catalysts are challenged by the difficulty of separation, difficulty of recycling and poor mechanical robustness. Consequently, a great amount of research is put into designing heterogeneous catalysts for otherwise homogeneous processes [3,4].

Here, we present the synthesis and use of N-doped carbon-encapsulated metal nanoparticles and their application as heterogeneous catalysts in different organic reactions. We for instant show the synthesis of heterogeneous catalysts based on the base metals, nickel and cobalt. The silylative pinacol coupling of arylaldehydes catalyzed by the easily accessible, heterogeneous base-metal catalyst is also demonstrated. Furthermore, the catalysts is applied in the olefin migration of allylarenes. The obtained 1-propenylarene motif is ubiquitous in Nature and frequently found in compounds displaying useful bioactivities. The catalysts can be recycled easily by magnetic filtration. Furthermore, some insight into the nature and reaction progress is disclosed. The catalysts are further characterized using a number of different techniques.

2. Experimental

All the reported materials were synthesized form commercially available chemicals. The encapsulated NiCo nanoparticles were prepared in different ways. In one method, the Ni and Co precursors are dissolved in methanol and precipitated with ethylenediaminetetraacetic acid (EDTA) under autogenous pressure in an autoclave.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.

We have tested the materials as catalysts in different reaction inclung silylative pinacol coupling and the olefin migration of allylarenes. Furthermore, we have characterized the materials with various techniques including SEM, STEM, XPS, XRF, BET and XRD among others.

3. Results and discussion

In our study, we found a good heterogeneous catalyst which consists of nickel and cobalt alloy nanoparticles encapsulated in nitrogen-doped carbon: Ni_1Co_1@NC. Figure 1 shows BF-TEM and HAADF-

STEM images of Ni_1Co_1@NC. The nanoparticles are approximately 10 nm in diameter and the overall material is predominantly comprised of nickel and cobalt in a 1:1 ratio with the third most prevalent element being carbon. Other ratios of nickel and cobalt, as well as the analogous pure metal materials, displayed inferior activity when compared to Ni_1Co_1@NC.

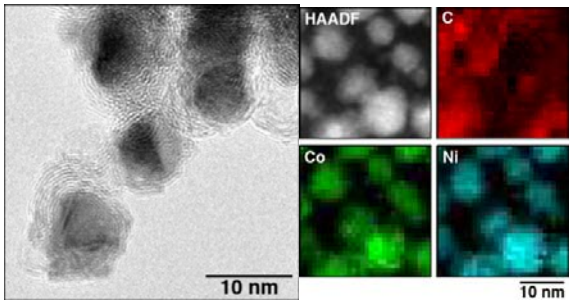
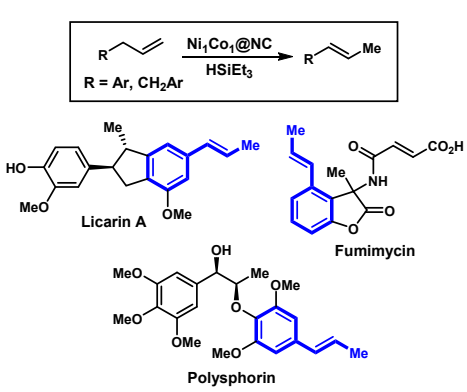
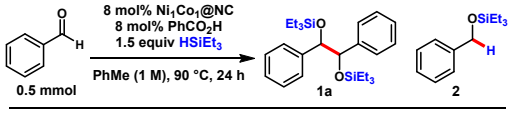


Figure 1. Ni_1Co_1@NC: BF-TEM and HAADF-STEM image along with the elemental distribution of C, Co, and Ni determined by EDX.

We showed the use of the easily prepared heterogeneous catalyst material for the migration of olefins, in particular allylarenes, see figure 2. The silylative pinacol coupling of arylaldehydes catalyzed by the heterogeneous base-metal catalyst is also demonstrated, see figure 2 [3]. The obtained results provided evidence for a reaction mechanism which is different from the classical pinacol coupling pathway [4].





Entry	Change from standard cond.	conv. [%]	Yield 1a [%]	Yield 2 [%]
1	none	>95	79	20
2	no Ni_1Co_1@NC	5	0	<4
3	no silane	5	0	0
4	no $PhCO_2H$	>95	54	38
5	reaction in air	90	66	13
6	neat	>95	77	23
7	heptane instead of PhMe	>95	75	25
8	70 °C instead of 90 °C	63	33	7
9	1.2 equiv $HSiEt_3$	60	47	13
10	2.5 equiv $HSiEt_3$	>95	72	22

[a] Conversion and yield are based on ^1H NMR analysis with the aid of an internal standard. d.r. of 1a was 53:47 in all cases. 8 mol% Ni_1Co_1@NC corresponds to 3.3 mg.

Figure 2. Application of catalyst in different reactions.

4. Conclusions

In summary, we demonstrated that a heterogeneous catalyst, based on the Earth-abundant metals nickel and cobalt, could facilitate olefin migration to produce highly valuable 1-propenylarenes. The catalyst material, consisting of metal alloy nanoparticles encapsulated in nitrogen-doped carbon, was readily prepared from cheap and commercially available precursors. Furthermore, we have developed an improved protocol for the carbon–carbon bond forming pinacol coupling in terms of simplicity, safety, and sustainability

References

1. B. Cornils, *J. Catal*. 216, 23–31 (2003).
2. F. Wang, et al.. *Angew. Chemie Int. Ed.* 2014, 53, 8645-8648.
3. S. Kramer, J. Mielby, K. Buss, T. Kasama, S. Kegnæs, *ChemCatChem.*, 2017, 9, 2930-2934.
4. S. Kramer, F. Hejjo, K. H. Rasmussen, S. Kegnæs, 2017 *submitted*.