

INCAT Industrial Catalysis and Adsorption Technology





+1=3

# DEPARTMENT OF MATERIALS, TEXTILES AND CHEMICAL ENGINEERING

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# INTRODUCTION

Nanotechnology - defined as Key Enabling Technology in Europe - plays an important role in our society, e.g., in medicine, in sports, in water treatment applications, in energy devices and is now also emerging in the field of catalysis. It strongly encompasses research and development to synthesize, control, and manipulate catalytic systems of enhanced or even novel properties. These properties can be attributed to the size of the nanomaterial which is ranged in one or more external dimensions from approximately 1 to 100 nm. [1]

Focusing on the catalysis of organic reactions, metal nanoparticles (MNPs, preferably below 10 nm) are frequently used to enhance the catalytic performance. However, their use as catalyst requires their stabilization against self-aggregation and leaching. This is particularly critical for heterogeneous catalysis applications where a robust linkage between the MNPs and the support would afford better performances in terms of catalyst recovery and re-use as well as avoiding product contamination.

#### **MANUFACTURING & MATERIALS** MEDICINE

## CATALYSIS

### **ENVIRONMENTAL**

### **ENERGY & ELECTRONICS**





## Why shifting towards 'nano' in catalyst design?

- The use of MNPs in catalytic reactions has brought superior efficiency in terms of activity and selectivity due to their high surface-to-volume ratio [2] and quantum confinement [3].
- The introduction of 'nano' enables the replacement of precious noble metals by catalysts tailored at the nanoscale and even by the use of non-noble metals, while preserving or outstanding the catalytic performance. As a result, the **process costs** could be **reduced** significantly.

Most advances in industrial heterogeneous catalysis are based on merely enhancing the catalytic activity of supported MNP catalysts (i.e., 1+1=2). Only little is known concerning their ideal characteristics due to a lack of fundamental knowledge about the **mechanism of the interactions**. Understanding metal-support and NP size effects are necessary to enable new and useful insights in order to further tune heterogeneous catalysts, and hence, will bring incremental advances (i.e., 1+1=3) in terms of catalytic performance to catalyzed chemical reactions in industry.

100

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60

3 50

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a 30

<u>ŏ</u> 20

10

• OH • • CO<sub>3</sub><sup>2</sup>

Α

# **RESEARCH FOCUS**

A missing link in current heterogeneous catalytic grafting designs is the lack of knowledge about the role of the support, and thus, the stabilization [4], on the catalytic performance. Therefore, this research focusses on these **metal-support interactions** as well as on **NP size** effects induced by e.g., varying the reduction temperature, the metal composition and NP structure [5].

### APPLICATIONS



# **STABILIZATION TYPES** [4] **STERIC ELECTROSTATIC**

### **METAL-SUPPORT EFFECTS**

- Effect of the resin functionality



- Effect of the hydrotalcite structure



### **NP SIZE EFFECTS**

Effect of the reduction temperature



Effect of the metal composition & the NP structure





Pd-NP PdCu-NP MgAlO / MgAlOH species

-SO<sub>3</sub>H

Figure 2:. Catalytic activity leaching and with the schematic proposed representation of five different Pd-NPs (1.0 wt%) @hydrotalcite catalysts. [7]

#### 18000 →Lewatit K2629 16000 Lewatit K1221 <mark>ු</mark> ි 14000 -Amberlite IRC748 <u>0</u> 12000 Lewatit TP260 $_{\rm H}^{2}$ 10000 J 8000 ີ່ <u>6000</u> $^{\pm}_{>}$ 4000 2000 25 15 20 10

Resin	Functionality	Hydrogen Generation Rate (L H <sub>2</sub> g <sup>-1</sup> Co min <sup>-1</sup> )	Co leaching (%)
Lewatit K2629	-SO <sub>3</sub> H	6.6	1.48
Lewatit K1221	-SO₃H	9.9	1.60
Amberlite IRC748	-CH <sub>2</sub> N(CH <sub>2</sub> COOH) <sub>2</sub>	7.0	0.96
Lewatit TP260	-CH <sub>2</sub> NHCH <sub>2</sub> PO(OH) <sub>2</sub>	9.4	1.52

Time (min)

Figure 3: The volume hydrogen gas produced per mol Cobalt as function of time, the Hydrogen Generation Rates and leaching values for four different Co-NPs (6.5 wt%) @resin catalysts.

Catalyst, K<sub>2</sub>CO<sub>3</sub>, DMF/H<sub>2</sub>O (1:1) 40°C. 3h [6 45 min [7]



C

-CH<sub>2</sub>N(CH<sub>3</sub>)<sub>3</sub>OH

PHARMACEUTICAL AND FINE CHEMICAL INDUSTRIES

SUZUKI-MIYAURA CROSS-COUPLING



3.5

2.5

1.5

0.5

Figure 1:. Catalytic activity with the schematic proposed representation of three different Pd-NPs (0.11 wt%) @resin catalysts. [6]

**HYDROGEN GENERATION** 

**ENERGY INDUSTRY** 



# CONCLUSIONS

Based on metal-support and NP size effects, an optimized catalyst design was proposed which allows us to tune and further enhance the catalytic performance at mild reaction conditions, resulting in lower process costs.

### **SUZUKI-MIYAURA CROSS-COUPLING**

### **HYDROGEN GENERATION**

• A strong acid functionality, co-catalyzing

the hydrolysis reaction.

- strong basic functionality, positively participating in the reaction mechanism.
- An uncalcined, co-precipitated structure, causing a high accessibility of the active centers.
- More active NPs are achieved at lower reduction temperatures.

### References



[1] Kung, H.H., et al., Nanotechnology and Heterogeneous Catalysis. In: Nanotechnology in Catalysis - Nanostructure Science and Technology. Springer, New York (2007) 1-11. [2] Domènech, B., et al., (2012) Bifunctional Polymer-Metal Nanocomposite Ion Exchange Materials, In: Ion Exchange Technologies. InTech, Rijeka (2012) 1-39. [3] Rabouw, F.T., et al., Topics in Current Chemistry (2016) 58, 1-30. [4] Cookson, J., Platinum Metals Reviews (2012) 56, 83–98. [5] Prechtl, M., et al., Nanotechnology Reviews (2013) 2, 577-595. [6] Van Vaerenbergh, B., et al., ChemCatChem (2017) 9, 451-457. [7] Van Vaerenbergh, B., et al., Applied Catalysis A – General (2018) 550, 236-244.

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FEBRUARY 6th, 2018