Transition metal nanoparticles on pyrrole-decorated sp^2 carbon allotropes for selective hydrogen isotopic exchange.

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Introduction

Compared to homogeneous catalysts, heterogeneous systems possess more attractiveness in the chemical industry because of

- Easier separation from the reaction products
- Lower amount of wastes
- Larger recyclability
- Lower toxicity and corrosiveness

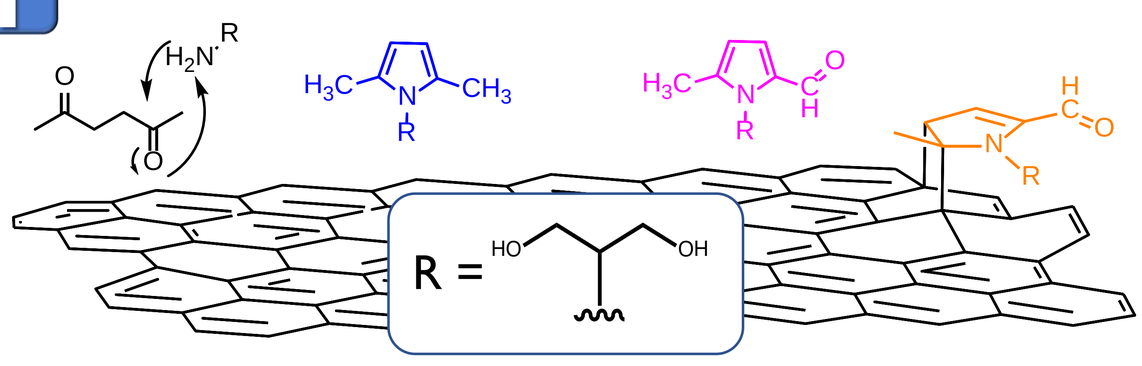
Preparation of supported metal nanoparticles requires often energy demanding techniques such as laser ablation, electrochemical reduction and high temperature heat treatments.

In this work we present a **facile** and **sustainable** method to functionalize multi-walled carbon nanotubes (MWCNTs) and exploit the novel surface reactivity to deposit Ruthenium nanoparticles.

Objectives

1. To functionalize multi-walled carbon nanotubes with the so-called "**pyrrole methodology**" with Serinol-pyrrole (SP). [1-3]
2. To employ **mild reducing** conditions in order to decorate the CNT-SP surface with Ruthenium nanoparticles.
3. To test the catalyst in the **selective deuteration** of quinoline.

1



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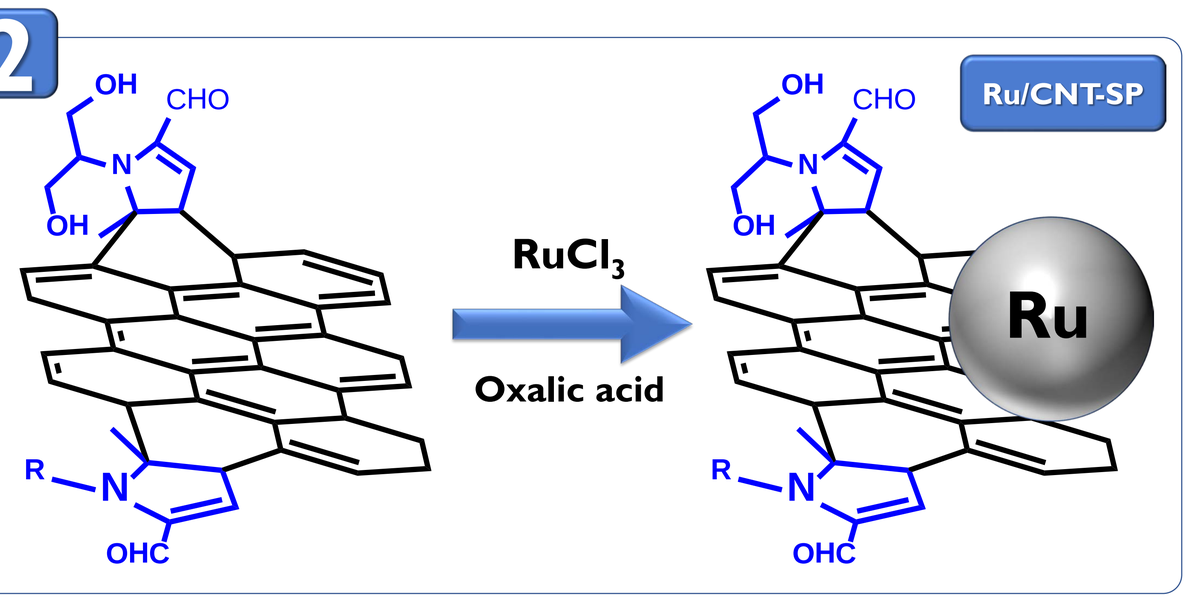

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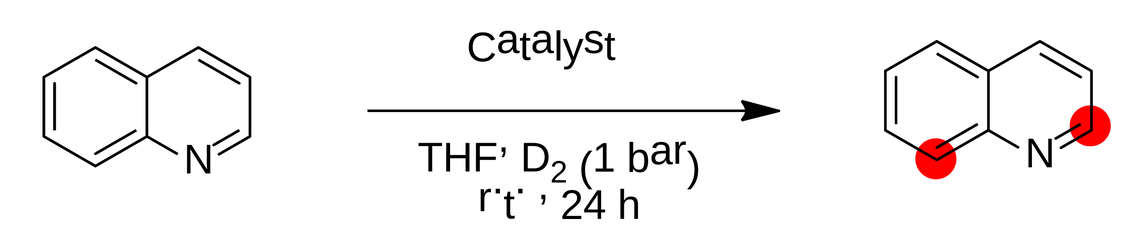
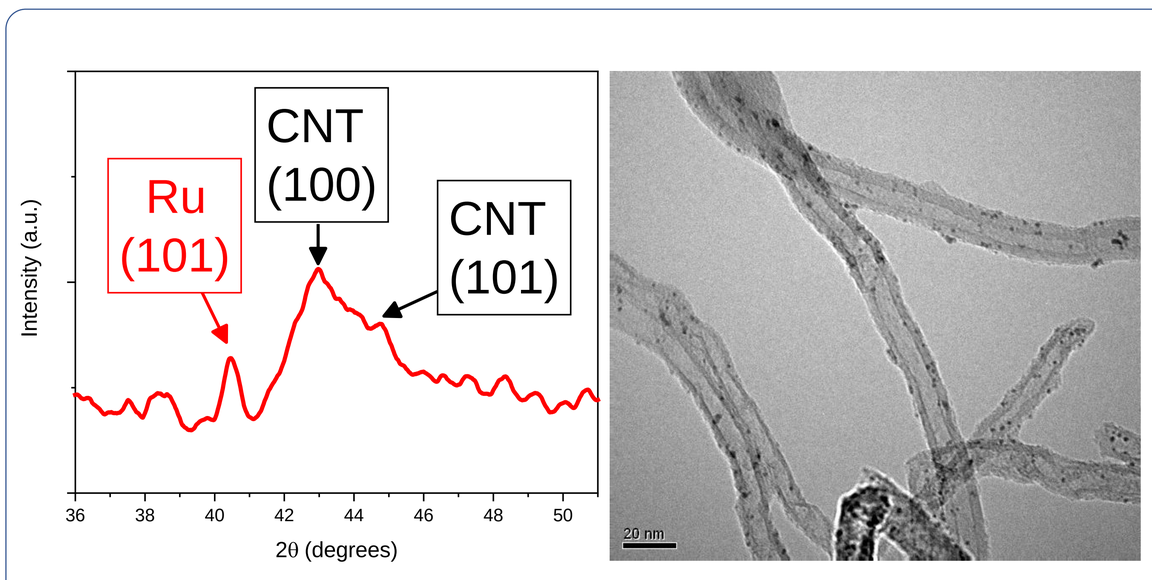


Results

Characterization of the Ru/CNT-SP

- X-Ray powder diffraction (**XRPD**) confirmed the presence of a **crystalline phase** of Ruthenium metal.
- High Resolution Transmission Electron Microscopy (**HR-TEM**) images showed a **good dispersion** of the metal nanoparticles, with an average dimension < 12 Å.



Hydrogen Isotopic Exchange (HIE) reaction

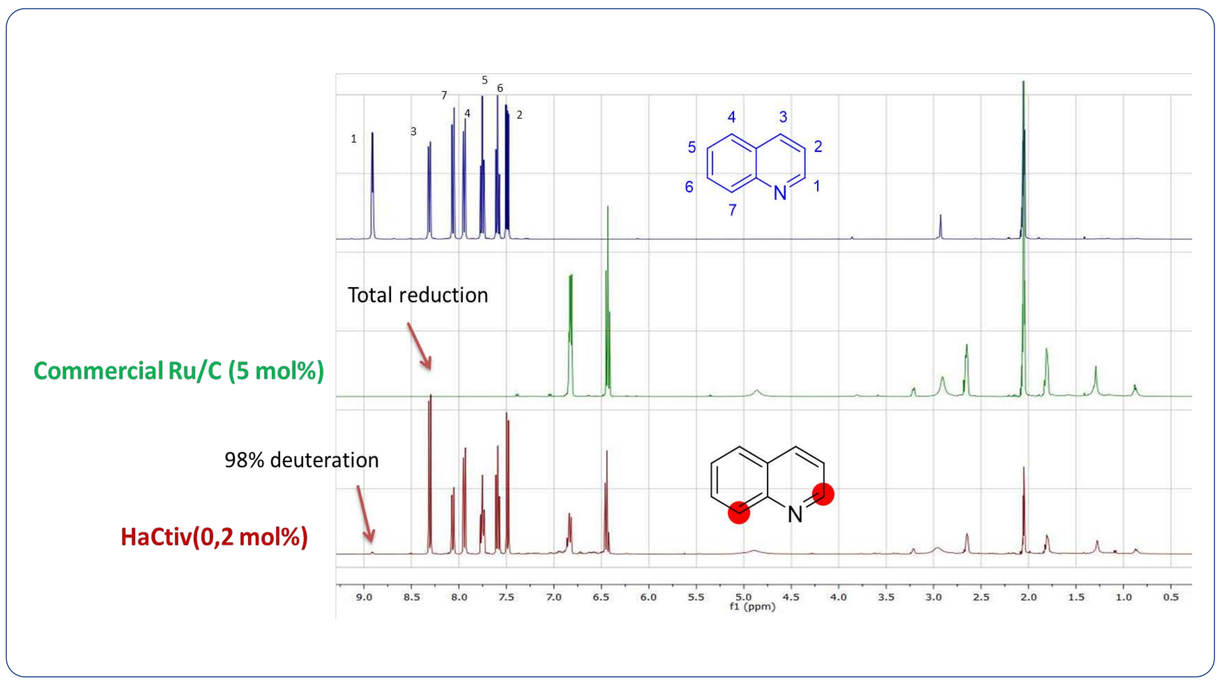
Proton Nuclear Magnetic Resonance (**H-NMR**) was used to determine the **conversion** and **selectivity** of the reaction.

Ru/CNT-SP catalytic properties for the HIE reaction are reported below:

- 98% of **conversion.**
- **Outstanding selectivity** in the deuteration of 1 and 7 positions of quinoline molecules.

The reaction was performed under **mild** conditions (1 bar D_2 at r.t.).

Commercial Ru/C was found to be not selective at all.



The results obtained in this work led to the filing of **two patent applications.**[4,5]

References

[1] V. Barbera, L. Brambilla, A. Milani, A. Palazzolo, C. Castiglioni, A. Vitale, R. Bongiovanni, M. Galimberti, Nanomaterials, 2019, 9, 44.

[2] M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini, RSC Adv., 2015, 5, 81142-81152

[3] D. Locatelli, V. Barbera, L. Brambilla, C. Castiglioni, A. Sironi, M. Galimberti, Nanomaterials, 2020 10(6), 1176

[4] Italian patent application no. 102020000020104, filed on August 13th, 2020

[5] Italian Patent Application n. 102020000020113 filed August 13th, 2020

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