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INTRODUCTION

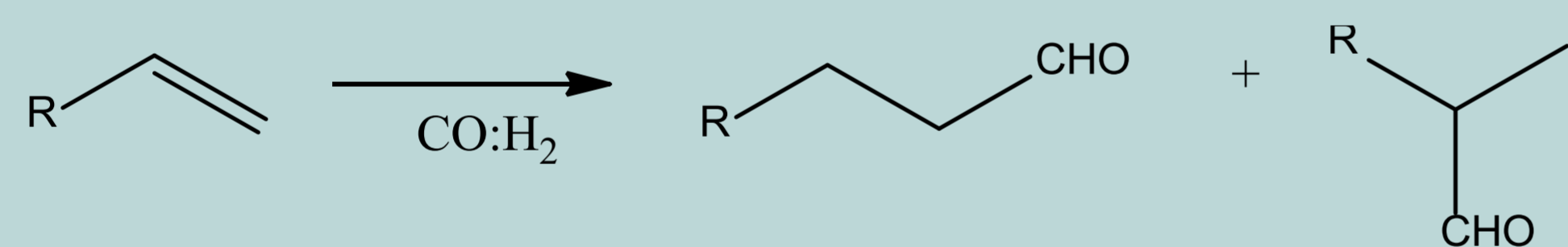
Hydroformylation is the transformation of olefins into aldehydes by adding H₂ and CO.¹ It is one of the most significant homogeneously catalyzed reactions relating to production scale, hence the need to boost heterogeneous catalysis to solve the problems of catalyst separation and recovery.^{2,3} These catalysts are composed of single atoms and nanoparticles with mainly metallic rhodium as active species; however, despite the significant role of phosphorus ligands in hydroformylation, little research has been done in the application of Rh phosphide nanoparticles in the reaction.^{4,5} Here, we describe a straightforward method for the formation of Rh₂P nanoparticles from a single precursor, as well as their application in liquid-phase hydroformylation and assessment via leaching and reusability tests.⁶

CATALYST PREPARATION

In this work, two type of materials have been synthesized: **Rh₂P@C** and **Rh@C**, the former was prepared at 5%, 1%, 0.5% and 0.3% metal loading, and the latter, for comparison purposes, at 5% and 1%. Active carbon was chosen as support for each of them, and as a rhodium source, a phosphorus rhodium complex was used for **Rh₂P@C** and a non-phosphorus rhodium complex for **Rh@C**. Nanoparticles were formed after solvent removal under reduced pressure and pyrolysis treatment.

CATALYTIC ACTIVITY

The materials' catalytic activity has been tested in the hydroformylation reaction (Scheme 1) with 1-hexene as substrate. The results revealed how positive the presence of P is in the reaction, since the yields obtained with **1%Rh₂P@C** were twice as good as **1%Rh@C** ones (Table 1). Besides 1-hexene, other olefins were assessed (Table 2) to confirm the suitability of **1%Rh₂P@C** for hydroformylation, resulting in especially good yields for styrene and propylene.



Scheme 1. General scheme of the hydroformylation reaction

Table 1. Catalytic performance of different catalysts in the hydroformylation of 1-hexene in reaction times of 5 hours

Catalyst	Yield (%)
1%Rh ₂ P@C	94
5%Rh ₂ P@C	49
0.5%Rh ₂ P@C	84
0.3%Rh ₂ P@C	74
1%Rh@C	45
5%Rh@C	3

Table 2. Hydroformylation substrate scope using **1%Rh₂P@C** as catalyst in 5 hours

Substrate	Yield (%)	Linearity (%)
1-Hexene	94	60
Styrene	99	21
Cyclohexene	51	100
1-octene	84	62
Propylene	98	50

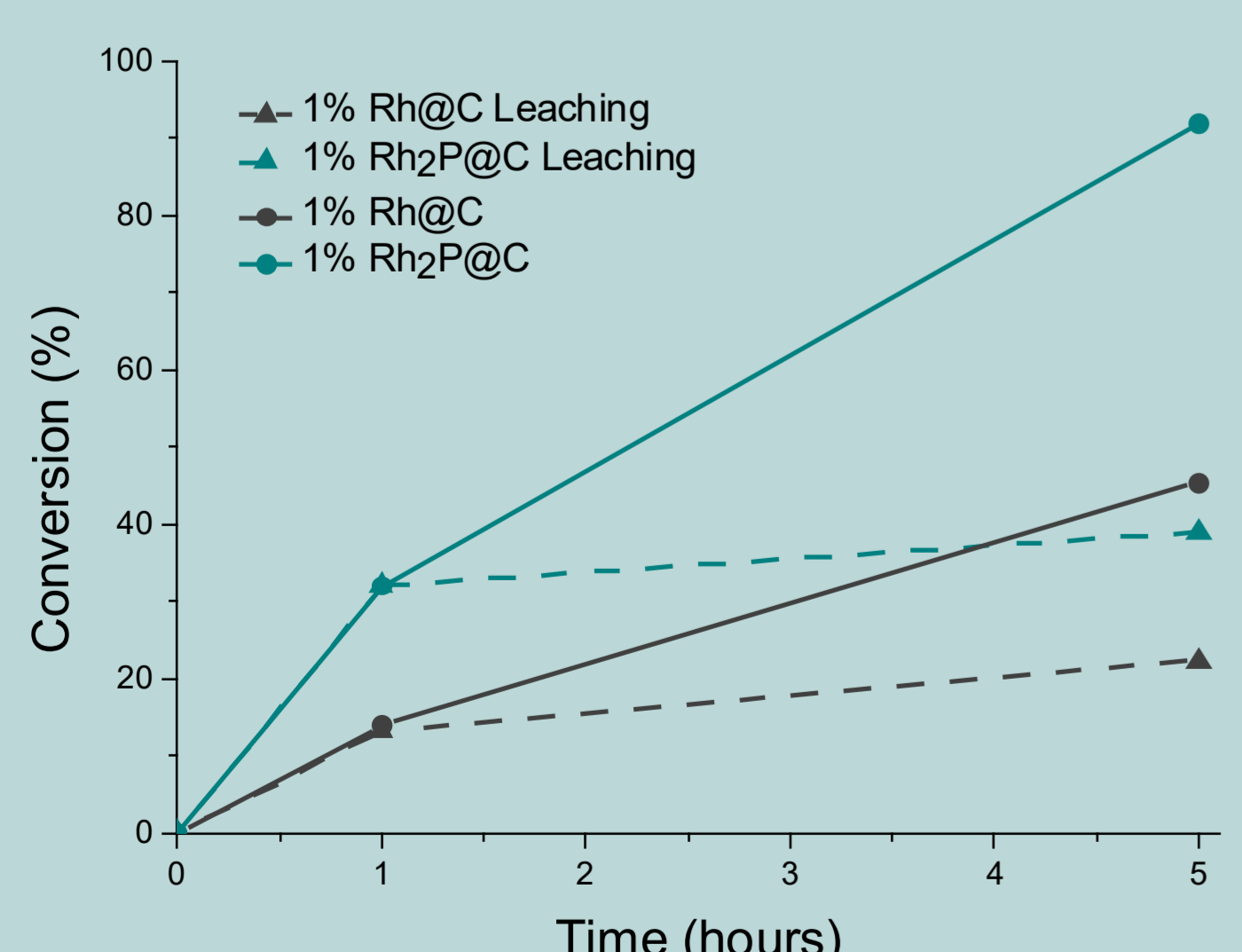


Figure 1. Reaction profiles for **1%Rh₂P@C** (green) and **1%Rh@C** (grey) and their filtrates

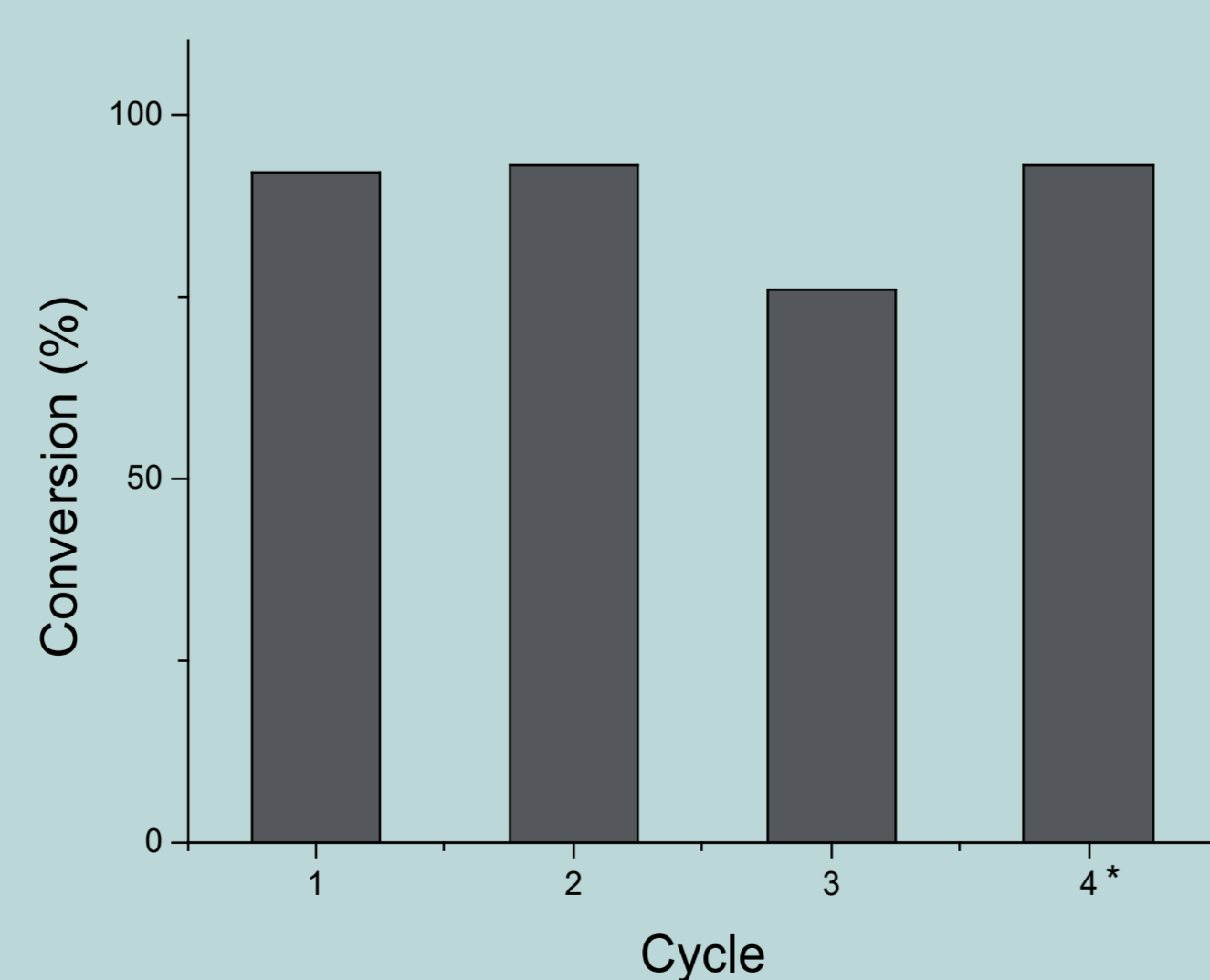


Figure 2. Product yields for **1%Rh₂P@C** over the course of four reaction cycles

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CHARACTERIZATION

Catalysts were characterized by using XRD, STEM and HRTEM. XRD diffractograms were measured for **5%Rh@C** and **5%Rh₂P@C**, and in the case of the latter diffractograms were also measured after catalysis. With STEM images, almost identical average particle sizes were obtained for **1%Rh₂P@C** and **1%Rh@C** and HRTEM images allowed lattice spacing measurements.

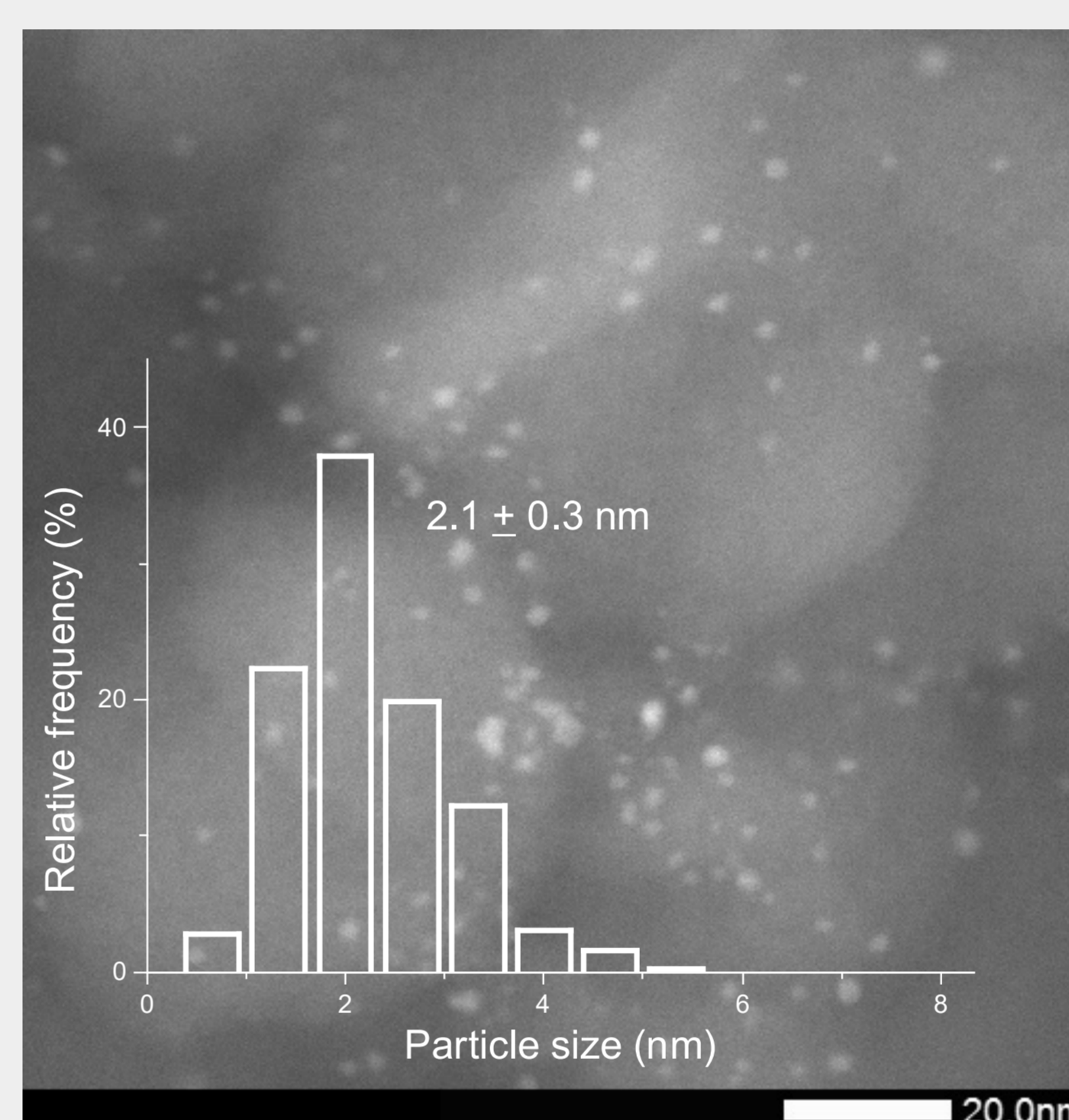


Figure 3. TEM image for **1%Rh₂P@C** and average particle size in white

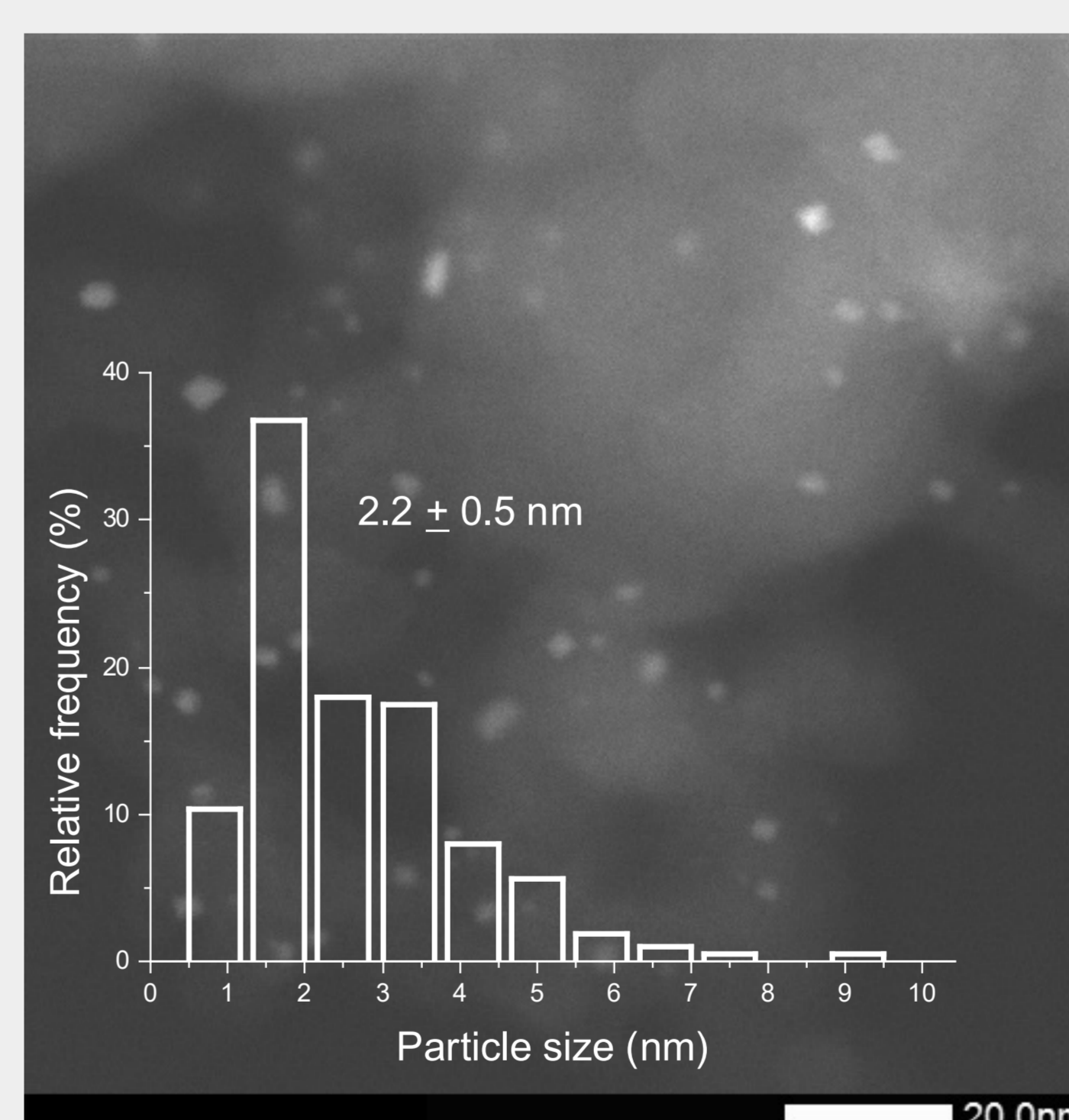


Figure 4. TEM image for **1%Rh@C** and average particle size in white

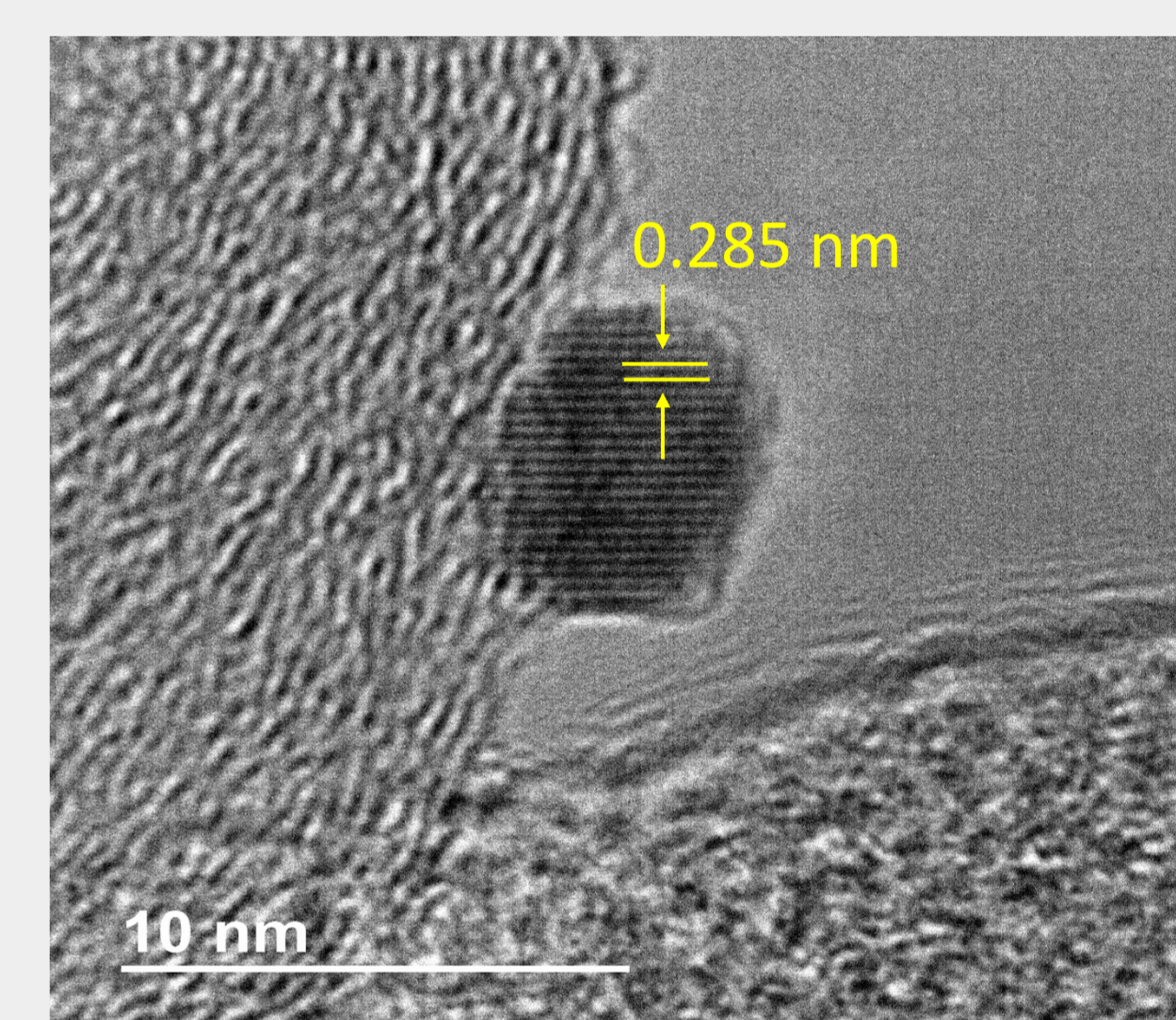


Figure 5. HRTEM of a **1%Rh₂P@C** nanoparticle

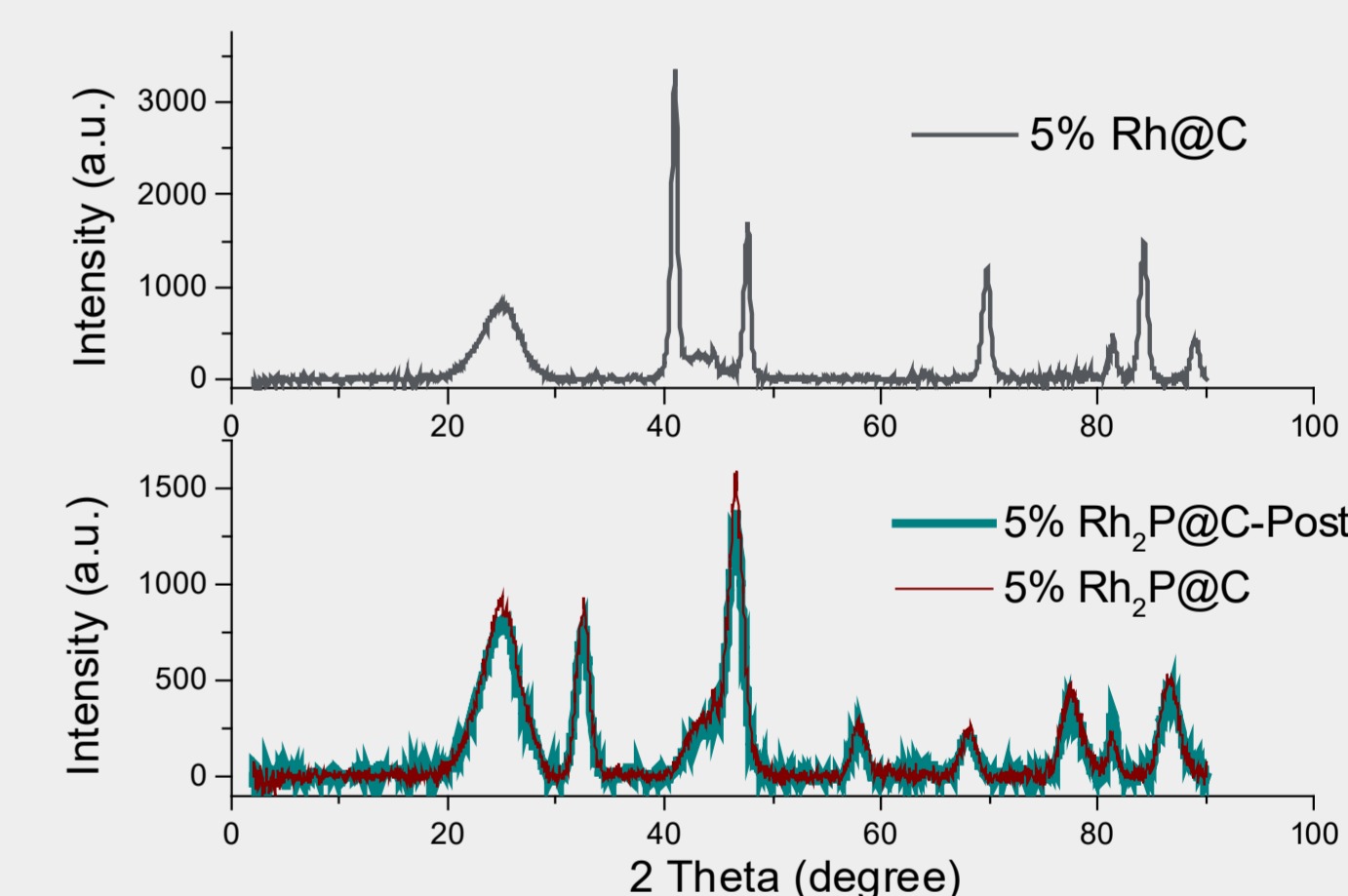


Figure 6. XRD diffractograms for **5%Rh@C** (grey), **5%Rh₂P@C** before (red) and after (green) catalysis

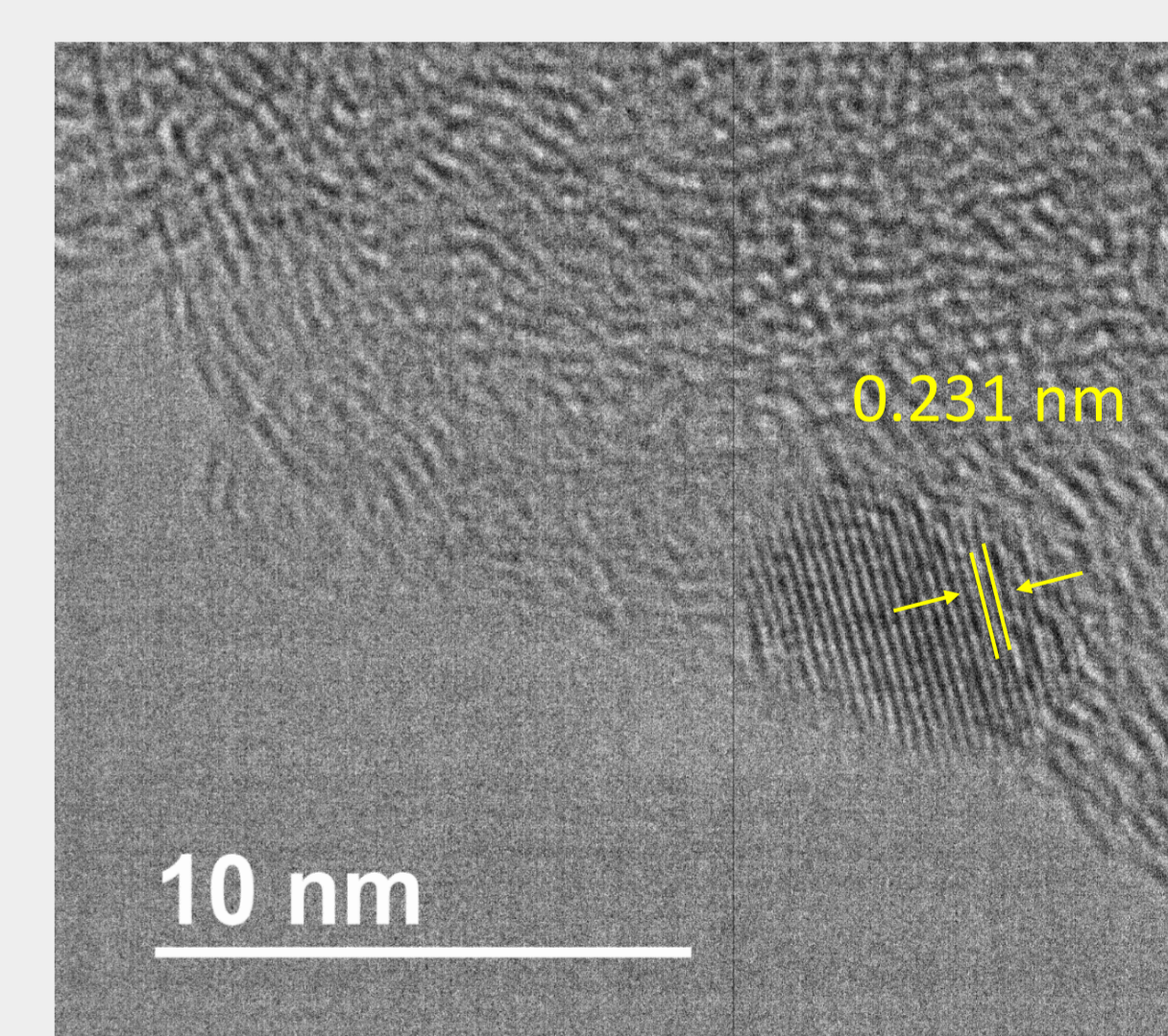


Figure 7. HRTEM of a **1%Rh@C** nanoparticle

CONCLUSIONS

To sum up, we have developed carbon-supported Rh₂P nanoparticles and tested their suitability for the liquid phase hydroformylation reaction with regards to metallic Rh nanoparticles. Materials have been characterized before and after catalysis, and their stability and reusability have been studied via leaching and reusability tests.

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