

Few-layer graphene as a new 2D support for selective hydrogenation reaction

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Catalysis is considered at the core of the success of modern chemistry and industrial development [1]. Indeed, catalysis participates in more than 80 % of the chemical transformations processes to produce food, energy, and commodities for human's day-life. In addition, catalysis also strongly participates to the environmental protection, i.e. off-gas cleaning, automotive exhaust depollution. The development of the new generation of catalysts goes along with the development of new supports which ensure the dispersion and stabilization of the deposited metal active phase [2].

Graphene, a single atomic layer of sp²-bonded carbon atoms with a honeycomb lattice arrangement has received an over increasing interest [3]. The few-layer graphene (FLG) defines the material constituted by an assembly of graphene layers for which the production and handling are easier than for a single-layer. Graphene and FLG display a relatively high external surface area which allows them to be efficiently employed as catalyst support.

The aim of the present work is to report the use of the FLG as support for palladium in the liquid-phase hydrogenation reaction. The catalytic results will be compared with those obtained on the carbon nanotubes-based catalyst.

The FLG used in this work was obtained by a mechanical exfoliation method of natural graphite following by an ultrasonication step in ethanol medium [4]. TEM micrographs indicate that the FLG is consisted with a relatively large sheet with size ranged between 0.1 to 2 μm (Fig. 1A) and is consisted with a graphene layers ranged from 2 to 15 (Figure 1B). The specific surface area of the FLG, measured by means of the liquid-phase adsorption of the methylene blue, is about 260 m². g⁻¹, which is similar to that was obtained with carbon nanotubes material. XPS analysis also indicates the presence of a relatively high number of oxygenated functional groups on the graphene surface which could help the anchorage and dispersion of the palladium active phase on the support surface similarly to that was observed with carbon nanotubes [5, 6]. Representative TEM micrographs of the Pd/FLG catalyst are depicted in Figure 2 and indicate the high dispersion of the palladium metal particles on the graphene surface (Fig. 2A) with an average particle size of around 5 nm (Fig. 2B). In some area of the catalyst few palladium particles with bigger size, i.e. 20 nm, are also observed.

The catalytic performance of the Pd/FLG and Pd/CNT catalysts for the selective hydrogenation of the C=C bond is presented in Figure 3. According to the results the Pd/FLG is more active and selective compared to the Pd/CNT. The high hydrogenation activity of the Pd/FLG could be attributed to the absence of inner channel in the FLG material unlikely to carbon nanotube. In the case of CNT some

metal particles could be localized inside the channel [7] and thus, are less accessible to the reactant leading to a lower activity and selectivity. Cycling tests carried out on the Pd/FLG catalyst confirm the complete absence of any deactivation indicating that no leaching problem has occurred on the catalyst during the test.

In conclusion we have shown that graphene and FLG, 2D material, can be efficiently used as support in the heterogeneous catalysis field. The high amount of the oxygenated functional groups presents on the support surface allows a relatively homogeneous dispersion of the metal particles while the high accessible external surface area of the support significantly increase the exposed metal active surface for performing the reaction.

References

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Figures

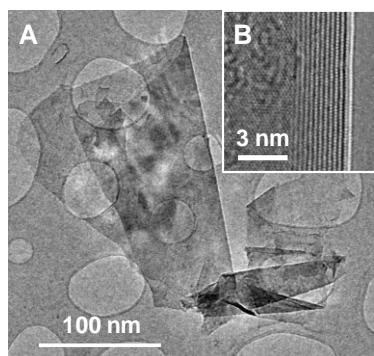


Figure 1. (A) TEM micrograph of the FLG. (B) HR-TEM of the FLG border containing 12 graphene layers.

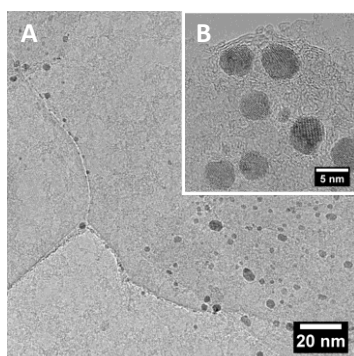


Figure 2. TEM micrographs of the Pd/FLG catalyst with different magnifications.

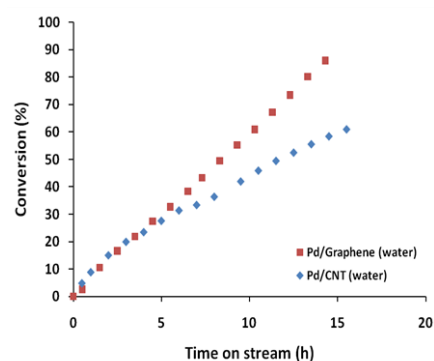


Figure 3. Selective hydrogenation catalytic activity of the Pd/FLG and Pd/CNT.