



# A novel catalyst containing palladium nanoparticles supported on poly(2-hydroxyethyl methacrylate)/CMK-1: Synthesis, characterization and comparison with mesoporous silica nanocomposite

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## ABSTRACT

A novel catalyst containing palladium nanoparticles supported on poly(2-hydroxyethyl methacrylate)/CMK-1 (Pd-PHEMA/CMK-1) was prepared, and its application was investigated as a heterogeneous catalyst in Heck coupling reaction. PHEMA/CMK-1 was prepared by in situ polymerization method and used as a support for palladium nanoparticles obtained through the reduction of palladium acetate by hydrazine hydrate. The structural and morphological characterizations of Pd-PHEMA/CMK-1 nanocomposite were carried out using XRD, FT-IR, BET, TGA, XPS, UV-vis, SEM and TEM techniques. This catalytic system exhibited good activity in cross-coupling reactions of aryl iodides, bromides and also chlorides with olefinic compounds in Mizoraki–Heck reactions in short reaction time and high yields. The catalytic activity of this purely organic hybrid catalyst was compared with Pd-PHEMA/MCM-48 to clarify the advantages of mesoporous carbon on mesoporous silica as support. The results showed that the activity and reusability of Pd-PHEMA/CMK-1 was much higher than Pd-PHEMA/MCM48 in Heck reaction.

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## 1. Introduction

The palladium catalyzed C–C coupling reactions belong to the most powerful processes for carbon–carbon bond formation. As most important representatives of this class of reactions, Heck coupling has to be noted [1–3]. These reactions are carried out in the presence of Pd catalysts involving ligands such as phosphines, amines, carbenes, dibenzylideneacetone (dba) and Schiffs bases [4–6]. However, the separation and recovery of homogeneous catalysts are not easy, and the resulting products are often contaminated by Pd metal. On the other hand, reusable heterogeneous catalysts are recently attracting much attention due to increasing international momentum for the development of an environmentally friendly reaction in terms of green chemistry [7].

In catalytic applications, a uniform dispersion of nanoparticles and an effective control of particle size are usually expected. However, nanoparticles frequently aggregate to yield bulk-like materials, which greatly reduce the catalytic activity and selectivity. Therefore, they must be embedded in a matrix such as polymer or macromolecular organic ligands [8,9]; or immobilized in the pores of heterogeneous supports, like ordered mesoporous silica

[10,11]. However, nanoparticle–polymer composites usually suffers from disadvantages such as absence of complete heterogeneity [12] and high temperature annealing which generally causes thermal degradation of organic polymers. On the other hand, although nanoparticle–mesoporous silica materials are completely heterogeneous, the hydrophilicity of these catalysts causes a reduction in the activity of such catalysts in organic reactions. Therefore, preparation of polymer hybrid catalysts based on mesoporous materials with a hydrophobe nature is interesting.

Mesoporous materials have received significant attention because of their promising applications in many fields such as catalysis, selective adsorption, sensors, and nanotechnologies owing to their excellent textural parameters such as huge surface area, large pore volume, large pore diameter, and interesting morphologies and topologies [13–17].

In late 1990s, ordered mesoporous carbons (OMCs) have been synthesized using hard-templating (HT) method [18–20], also referred to as nanocasting due to the fact that the final product is an inverse replica of the template used. Since the beginning, ordered mesoporous silicas (OMSs) have been utilized as hard templates for the synthesis of OMCs mostly because of easily tunable porosity in these materials and variety of morphologies available, e.g., MCM-41, MCM-48, SBA-15, SBA-16, and FDU-1. According to HT strategy, OMCs are obtained by filling the pores of siliceous templates with carbon precursors followed by their carbonization

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