



# Organometal-bridged PMOs as efficiency and reusable bifunctional catalysts in one-pot cascade reactions

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## ABSTRACT

Two bifunctional catalysts with two kinds of organometals incorporated into the periodic mesoporous organosilica (PMO) supports, denoted as Rh/Pd@PMO(Ph) catalyst and Fe/Cp\*Rh@PMO(Et) chiral catalyst, were synthesized by surfactant directed co-condensation between phenyl (Ph)- or ethyl (Et)-bridged and organometal-bridged silanes. Two bifunctional catalysts exhibited high activities and selectivities and even high ee values in one-pot two-step cascade reactions comprised Rh(I)-catalyzed methylenation and Pd(II)-catalyzed Heck reaction, or Fe(III)-catalyzed hydrolysis and Cp\*Rh-catalyzed asymmetric hydrogenation. The promoting effects from the ordered mesoporous structure, the coordination model, and the synergic effect between two kinds of active sites were discussed based on the detailed characterizations. Their catalytic efficiencies were comparable with the corresponding homogeneous catalysts and could be easily recycled and used repetitively, which could greatly reduce the cost and diminish the environmental pollutions from heavy metal ions.

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## 1. Introduction

Since the discovery of M41S, organic–inorganic composite materials with ordered and open porous structure have been widely studied owing to their potential applications in catalysis, adsorption, separation, etc., most studies have devoted to designing mesoporous organic–inorganic hybrid silicas [1–4]. Organic groups including methyl, ethyl, phenyl, biphenyl and amine have been successfully incorporated into ordered mesoporous silicas through either grafting the organotrialkoxysilanes  $\text{RSi}(\text{OR})_3$  or the direct co-assembly of organo-bridged silanes, resulting in the organic groups terminally bonded to the pore surface [5,6] or the periodic mesoporous organosilica (PMO) with organic groups as the integral part of the pore walls [7–11]. Learning from those achievements, we developed a facile approach to design immobilized homogeneous catalysts with combined advantages from both the homogeneous catalysts (e.g., high activity and selectivity) [12,13] and the heterogeneous catalysts (e.g., easy recycle and reuse) by either grafting organometals onto pore surface [14,15] or incorporating organometals into silica walls of the mesoporous channels [16,17]. The chiral organometal catalysts were also successfully

grafted onto mesoporous silica supports, which exhibited high activities and even ee values in various asymmetric reactions [18]. More recently, we also synthesized a new class of heterogenized homogeneous catalysts by immobilizing organometals onto the phenol–formaldehyde resin with ordered mesoporous structure [19].

As an expressly practical science, synthetic organic chemistry counts as one of its primary aims at the invention of efficient, rapid and economical strategies to gain valuable chemical substances [20,21]. One-pot cascade or tandem organic reactions have received great attentions since they could simplify the operation procedure in intermediate product purification or detections and also diminish the environmental pollution [22,23]. The key stone to realize the one-pot cascade or tandem organic reactions is the design of powerful multiple-functional catalysts, which allow to alleviating dependency on strictly reduplicative processes [24–26]. To date, most cascade and tandem organic reactions are conducted in homogeneous catalyst systems [27], which usually display inherent disadvantages in difficult recycle, leading to the high cost and even the environmental pollutions from heavy metal ions. Meanwhile, the cross-interference between different kinds of active sites also frequently occurs in homogeneous catalytic systems [28]. Heterogeneous catalysts are easily recycled and used repetitively, however, they usually display poor activities and selectivities due to the enhanced steric hindrance and the changed chemical micro-environment of active sites [29,30]. Our strategy for the design of heterogeneous multiple functional catalysts focuses on the

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