



# Nanospace constraints in mesoporous silica carriers—A factor of critical importance in promoting the catalytic activity of supported ruthenium (II) complex with hemilabile phosphine ligand

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## ABSTRACT

Various mesoporous silica materials (FSM-16, HMS, SBA-15) aluminated via direct procedure or by a post-synthesis treatment, differing in the manner of Al distribution between the external surface and the mesoporous network, were employed for the immobilization of  $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ru}(\eta^3\text{-DPVP})(\eta^1\text{-DPVP})]^+$  (DPVP =  $\text{PPh}_2\text{CHCH}_2$ ) complex. The catalysts of similar loading (ca. 5 wt.%) of Ru-species were prepared by means of cation exchange. The samples were characterized with XRD, XPS, MAS NMR,  $\text{N}_2$  adsorption/desorption techniques and quantum chemical calculations, and tested in the liquid phase hydrogenation of phenylacetylene. Two binding modes of Ru species were identified: (i) at the surface free of spatial constraints, with the participation of the hemilabile ligand in the electrostatic attraction and (ii) in the limited space of narrow mesopores, via peripheral areas of Ru coordination sphere, leaving hemilabile phosphine exposed to the reaction medium. It has been demonstrated that the latter location is a prerequisite of high catalytic activity of the supported system, while the former destroys the catalytic action.

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## 1. Introduction

Homogeneous catalysis plays an important role in a number of large-scale industrial chemical processes. However, problems in separating homogeneous catalysts from the product(s), recovery and recycling of the catalysts, as well as environmental issues create demand for heterogeneous catalysts with comparable performance. The heterogenization of homogeneous catalysts is a very convenient way of combining the advantages of the homogenous catalysts with those of heterogeneous ones. It may be accomplished by immobilization of transition metal complexes on suitable porous material, and can lead to a new class of systems whose catalytic properties are determined by both the catalyst and the host.

Complexes of hemilabile ligands [1–12] are of current interest because of their potential application in molecular activation, homogeneous catalysis, and small molecular sensing [13]. The phosphaaallyl cationic ruthenium (II) complex  $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ru}(\eta^3\text{-DPVP})(\eta^1\text{-DPVP})]^+$  (DPVP =  $\text{PPh}_2\text{CHCH}_2$ ), abbreviated as  $(\text{RuL})^+$ , used in our previous studies [14,15], belongs to this class of complexes. As shown in Fig. 1 it contains two diphenylvinylphosphine

ligands ( $\eta^3\text{-DPVP}$ ) and ( $\eta^1\text{-DPVP}$ ) bound to the metal center. One of them ( $\eta^3\text{-DPVP}$ ), is substitutionally labile and “opens” while used in catalytic reaction, providing a coordination site for an incoming substrate, while the other group ( $\eta^1\text{-DPVP}$ ), remains firmly bound to the ruthenium center. The presence of hemilabile ligands in a complex may induce transformations of reactants that otherwise would not occur. The complex is used in the form of hexafluorophosphate salt  $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ru}(\eta^3\text{-DPVP})(\eta^1\text{-DPVP})]\text{PF}_6$ ,  $[(\text{RuL})^+(\text{PF}_6)^-]$ , enabling the heterogenization via ion exchange method which proved to be one of the most useful. This method, applicable to systems in which supported species appear in an ionic form and the support possesses appropriate exchange sites, allows the immobilization of readily available complexes and avoids the tedious and often very difficult task of ligand modification.

The discovery of ordered mesoporous silica materials such as MCM-41, HMS, FSM-16, SBA-15 families, characterized by hexagonal arrays of uniform pores with adjustable diameters in the mesopore range, introduced new opportunities for designing novel catalytic systems involving number of transition metals complexes [16–18]. Mesoporous silicas can acquire cation exchange properties by partial substitution of  $\text{Si}^{4+}$  ions with  $\text{Al}^{3+}$  in the framework. Recently, we have applied the aluminated HMS ( $\text{Si}/\text{Al} = 10, 20, \text{ and } 40$ ) supports for immobilization of  $(\text{RuL})^+$  by ion exchange procedure [14,15]. In the obtained novel catalysts the cationic ruthenium

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