

Olefin cyclopropanation and insertion into O–H bonds mediated by copper(I) and palladium(II) covalently anchored to silica xerogels

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Abstract

Copper(I) and palladium(II) ligated to pyrazolylpyridine bearing a tethered (trimethoxysilyl)propyl group in position 4 of the pyrazole ring were chemically bonded to silica via a sol–gel process. The textural properties of the materials (specific surface area, porous volume, and pore size distribution) were characterized by nitrogen adsorption–desorption isotherms, mercury porosimetry, and TEM analysis. The hybrid materials were tested as catalysts in olefin cyclopropanation and as potential chemoselective catalysts in the reaction with unsaturated alcohols (double bond versus –OH group), with ethyl diazoacetate as a carbene precursor, and compared with the corresponding homogeneous complexes.

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Keywords: Pyrazolylpyridine; Cyclopropanation; Insertion; Sol–gel; Xerogel

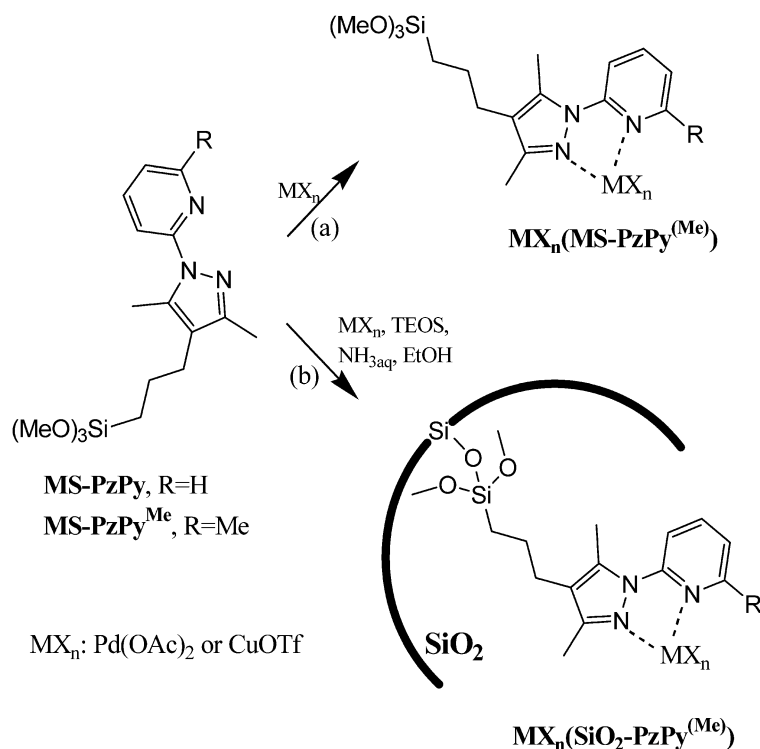
1. Introduction

Heterogeneous catalysis is generally widely preferred for industrial applications thanks to the well-known advantages of easier product–catalyst separations and recovery of the catalyst process and, often, to the enhanced stability of the catalyst. But in terms of selectivity, homogeneous catalysis usually provides better results. The grafting of homogeneous catalysts to a solid support seems the ideal combination for achieving the advantages of both heterogeneous and homogeneous catalysis, allowing the development of more environmentally friendly and economical processes with potential applications in industry [1]. Furthermore, covalently linking a homogeneous catalyst to silica (a support that is thermally, chemically, and mechanically resistant, with a well-defined structure) is the best way to limit metal leaching and sintering, although it implies first the synthesis of silylated catalyst precursors, which often proves to be laborious.

It is known that the activity of immobilized molecular catalysts may be remarkably affected by the nature of the support. It is apparent that development of heterogeneous processes relies on our ability to design diverse and specifically customized support materials. From this point of view, sol–gel chemistry is a versatile route to tailored, organically modified silica. This process is based on the hydrolysis and condensation of monomeric precursors, typically silicon alkoxides, leading to the formation of a three-dimensional porous network [2]. According to the cogelation sol–gel process proposed by Schubert et al. [3], Heinrichs et al. [4,5] and Lambert et al. [6–8] used this method to synthesize Pd/SiO₂, Ag/SiO₂, Cu/SiO₂, Pd–Ag/SiO₂, and Pd–Cu/SiO₂ cogelled xerogel catalysts. Further thermal treatments of cogelled xerogel catalysts gave highly dispersed palladium, silver, or copper nanoparticles in Pd/SiO₂, Ag/SiO₂, or Cu/SiO₂ catalysts and alloy nanoparticles in Pd–Ag/SiO₂ and Pd–Cu/SiO₂ catalysts. These metallic nanoparticles are trapped in microporous silica particles with a finely controlled texture. In a previous work [9], covalently bonded palladium organometallic complexes based on a series of silylated β-diketonate ligands were encapsulated in silica

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Scheme 1. (a) Preparation of Pd- or Cu-based homogeneous catalysts and (b) heterogenization via a sol-gel process.

particles according to the same cogelation sol-gel method. After thermal treatments, these samples contained small palladium particles with diameters of about 3.5 nm located inside silica particles exhibiting a monodisperse microporous distribution. The silylated β -diketonate ligands had a large influence on the textural properties of cogelled catalysts. Indeed, by changing the nature of the silylated β -diketonate ligand, it is possible to tailor textural properties such as pore volume, pore size, and surface area [9]. Furthermore, in all metallic cogelled xerogel catalysts, the complete accessibility and activity of the metallic sites through the microporous network were experimentally established and verified in a typical heterogeneous gaseous reaction, the catalytic hydrodechlorination of 1,2-dichloroethane, an important reaction for the treatment of chlorinated industrial wastes [4–9]. Finally, it was shown in a previous paper [10] that the very particular structure of those catalysts makes it possible to avoid diffusional limitations. Indeed, in metallic xerogel catalysts, to reach active sites, reactants must first diffuse through large pores located between aggregates of SiO_2 particles and then through smaller pores between those elementary particles inside the aggregates. Finally, they diffuse through micropores inside the silica particles. It was shown that there is no problem for mass transfer at each of the three levels. The Weisz modulus, which compares the observed reaction rate with the diffusion rate, has a value much smaller than 1 at three discrete levels: (i) macroscopic pellet, (ii) aggregate of silica particles, (iii) elementary silica particle containing an active metallic crystallite. So there are no pore diffusion limitations in the gaseous phase.

Recently, the synthesis of a new series of pyrazolylpyridine derivatives [11,12] bearing a tethered trialkoxysilyl group was reported, and it was suggested that they could be good potential nitrogen-based ligands for the heterogenization of homogeneous catalysts onto silica xerogel. Here the heterogenization of palladium(II) acetate and copper(I) triflate (CuOTf) via a sol-gel process mediated by the two following ligands is described (Scheme 1): 2-[4-[3-(trimethoxysilyl)propyl]-3,5-dimethyl-1H-pyrazol-1-yl]pyridine (MS-PzPy) and 2-[4-[3-(trimethoxysilyl)propyl]-3,5-dimethyl-1H-pyrazol-1-yl]-6-methylpyridine ($\text{MS-PzPy}^{\text{Me}}$). All of these hybrid organic-inorganic materials were characterized to determine their textural properties and tested in different reactions such as olefin cyclopropanation [13–16] and chemoselective insertion into the O–H bond of unsaturated alcohols, which is also called etherification [13,17].

The development of new methods for the efficient and selective preparation of cyclopropanes is of great interest in organic chemistry [18–22] because of the frequent existence of such structures in biologically active compounds [23] and their role as valuable synthetic intermediates. Furthermore, the reaction of acceptor-substituted carbene complexes with alcohols to yield functionalized ethers is a valuable alternative to other etherification reactions.

In the last four decades, many catalytic systems used to promote these kinds of reactions have proved successful on a laboratory scale, but few have been industrialized. Because of the inherent advantages of heterogeneous catalysts over homogeneous catalysts, a great deal of effort has been de-

Table 1
Synthesis operating variables to prepare heterogeneous xerogel catalysts

Sample	n_M	n_L	n_L/n_{TEOS}	n_{H_2O}	n_{EtOH}	H	R	% _{exp}
Pd(OAc) ₂ (SiO ₂ -PzPy)	0.244	1.00	0.03	214	428	5	10	1.4
CuOTf (SiO ₂ -PzPy) ^a	0.818	1.25	0.03	211	428	5	10	– ^b
CuOTf (SiO ₂ -PzPy)	0.818	3.17	0.08	211	428	5	10	1.3
CuOTf (SiO ₂ -PzPy ^{Me})	0.818	1.25	0.03	216	428	5	10	1.5

n_M , moles of metal (mmol); n_L , moles of silylated ligand MS-PzPy or MS-PzPy^{Me} (mmol); n_{TEOS} , moles of TEOS (mmol); n_{H_2O} , moles of water (mmol); n_{EtOH} , moles of ethanol (mmol); H , hydrolysis ratio; R , dilution ratio; %_{exp}, actual metal loading in the hybrid organic-inorganic material.

^a This sample was not used in this study because no gelification occurred.

^b Not measured.

voted to the development of heterogeneous catalysts that can promote selective organic reactions.

2. Experimental

All preparations and manipulations were carried out under an oxygen-free argon atmosphere with conventional Schlenk techniques. Argon was purified by passage through columns of BASF R3-11 catalysts and 4-Å molecular sieves. The solvents were dried and degassed before use.

2.1. Preparation of silylated pyrazolylpyridine ligands

The silylated pyrazolylpyridine ligands 2-[4-[3-(trimethoxysilyl)propyl]-3,5-dimethyl-1*H*-pyrazol-1-yl]pyridine (MS-PzPy) and 2-[4-[3-(trimethoxysilyl)propyl]-3,5-dimethyl-1*H*-pyrazol-1-yl]-6-methylpyridine (MS-PzPy^{Me}) (Scheme 1) were prepared as described in [11].

2.2. Catalyst preparation

2.2.1. Homogeneous catalysts [Scheme 1, path (a)]

Palladium or copper complexes of silylated pyrazolylpyridine, Pd(OAc)₂(MS-PzPy), CuOTf(MS-PzPy), and CuOTf(MS-PzPy^{Me}), were generated in dichloromethane by the addition of the metal salt to a solution of the ligand. So a suspension of 10⁻⁵ mol of palladium(II) acetate or copper(I) triflate, 1.1 × 10⁻⁵ mol of silylated pyrazolylpyridine ligand in 0.4 ml of dichloromethane was stirred for 30 min under an anhydrous argon atmosphere. The solvent was evaporated under vacuum, and the solid residue was utilized without further purification.

2.2.2. Heterogeneous catalysts [Scheme 1 path (b)]

The synthesis operating variables of the gels are listed in Table 1. Copper(I) triflate or palladium(II) acetate was dissolved for 30 min in 13 ml of ethanol containing an excess of the silylated ligand to allow complexation and gelling. After the addition of tetraethyl_orthosilicate (TEOS), a 0.18 N NH₃ aqueous solution in 10 ml of ethanol was added with vigorous stirring. The hydrolysis ratio, that is, the molar ratio $H = [H_2O]/([TEOS] + \frac{3}{4}[L])$, where L is the trialkoxysilylated ligand, and the dilution ratio, that is, the molar ratio

$R = [ethanol]/([TEOS] + [L])$, were kept constant at values of 5 and 10, respectively, for all samples. The vessel was then tightly closed and heated to 80 °C for 10 days (gelling and aging [2]). The wet gels were dried under vacuum according to the following procedure: the flask was opened and put into a drying oven at 80 °C, and the pressure was slowly decreased, to prevent gel bursting, to reach a minimum value of 1200 Pa after 90 h. The drying oven was then heated at 150 °C for 72 h. The resulting samples were xerogels [2].

2.3. Characterization of heterogeneous catalysts

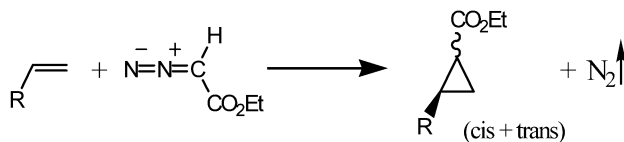
Nitrogen adsorption-desorption isotherms were measured at 77 K on a Fisons Sorptomatic 1900 after outgassing for 24 h at ambient temperature. After a 2-h outgassing at ambient temperature, mercury porosimetry measurements were performed with sample monoliths and a manual porosimeter from 0.01 to 0.1 MPa and a Carlo Erba Porosimeter 2000 from 0.1 to 200 MPa.

Samples were examined by transmission electron microscopy (TEM) with a Philips CM100 microscope. First, to strongly increase the contrast between silica and metallic nanoparticles, samples were calcined and reduced. The calcination conditions were as follows: each sample was heated to 400 °C at a rate of 120 °C h⁻¹ under flowing air (0.02 mmol s⁻¹); this temperature was then maintained for 12 h in air (0.1 mmol s⁻¹). The reduction conditions were as follows: each sample was heated to 350 °C at a rate of 350 °C h⁻¹ under flowing H₂ (0.23 mmol s⁻¹) and maintained at this temperature for 3 h (same flow). Afterward, all samples were impregnated with an epoxy resin (EPON 812) to which an amine was added to serve as a hardener. Hardening went on for 72 h at 60 °C, and 60-nm slices were then cut up with a Reichert-Jung Ultracut E Microtome. Finally, these slices were put on a copper grid.

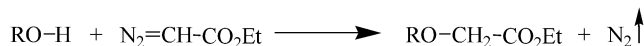
2.4. Catalytic experiments

Styrene and cyclooctene were freshly distilled under anhydrous argon from CaH₂. Alcohols and ethyl diazoacetate (EDA) were purchased from Aldrich and used without any further purification. Yields were determined by gas chromatography with a Varian Star 3400CX instrument and on a capillary FFAP column (15 m). Olefin cyclopropanation

Cyclopropanation:



O-H insertion:



Scheme 2. Addition of carbene by degradation of ethyl diazoacetate mediated by transition metal-based catalysts.

and chemoselective insertion into the O–H bond of unsaturated alcohols with EDA as a carbene precursor are shown in Scheme 2.

2.4.1. General procedure for the homogeneous medium

Five milliliters of olefin or alcohol was added in the homogeneous medium, which was composed of 10^{-5} mol of palladium(II) acetate or copper(I) triflate and 1.1×10^{-5} mol of silylated pyrazolylpyridine ligand. Under vigorous agitation, 2.2 mmol of EDA in 1 ml of olefin or alcohol was added dropwise with a syringe pump over a period of 3 h. The ratio EDA/M, where M is either copper(I) triflate or palladium(II) acetate, was equal to 220. The evolution of the reaction was followed by volumetric measurement of the nitrogen evolved. After all EDA was consumed, the resulting solution was analyzed by gas chromatography, and the reaction products were identified by comparison with authentic samples.

2.4.2. General procedure for the heterogeneous medium

Heterogeneous catalysts, $\text{Pd}(\text{OAc})_2(\text{SiO}_2\text{-PzPy})$, $\text{CuOTf}(\text{SiO}_2\text{-PzPy})$, and $\text{CuOTf}(\text{SiO}_2\text{-PzPy}^{\text{Me}})$, were crushed with a mortar and sieved between 250 and 500 μm meshes. From highly split hybrid organic–inorganic materials, a suspension of 10^{-5} mol of supported complex in 5 ml of olefin or alcohol was realized. EDA (2.2 mmol) in 1 ml of olefin or alcohol was added with the use of a syringe pump with vigorous stirring over a 6-h period. The ratio EDA/M, where M is either copper(I) triflate or palladium(II) acetate, is equal to 220. The evolution of the reaction was followed by volumetric measurement of the nitrogen evolved. When nitrogen evolution stopped, the resulting solution was analyzed by gas chromatography as above.

3. Results and discussion

3.1. Immobilization of catalysts

The sol–gel route requires the control of all operating variables governing the process, especially the kinetics of the concomitant hydrolysis and condensation reactions of the silica precursors [2,24]. Indeed, it was demonstrated

that the prior determination of these variables, which influenced the kinetics of one or both reactions, proved to be crucial to the control of the microstructure of the final material. The solvent, the concentration of the reactants (especially the hydrolysis ratio, H , and the dilution ratio, R [2]), the temperature, the reaction time (aging and drying), and the nature of the precursors (especially the nature of the alkoxides [25]) were knowingly chosen in accordance with previous works [6,7], to obtain silica xerogels with a finely controlled texture.

The impact of the coordinating moiety (in this study, the pyrazolylpyridine ligand) on the gelation process is actually not well understood. Nevertheless, a previous study concerning another series of bidentate ligands, silylated β -diketonate ligands, showed that the nature of the ligand, especially its steric hindrance, strongly influences the textural properties of the gel, that is, silica particle size, porous volume, specific surface area, and active species dispersion, and is important for the fine control of the texture [9].

In this work, the first step of the process consists of mixing in ethanolic medium the silica precursors (tetraethylorthosilicate, TEOS, and the silylated pyrazolylpyridine ligand), the metallic salt (palladium(II) acetate or copper(I) triflate), and an aqueous ammonia solution. All synthesis operating variables are listed in Table 1. The major advantage of this cogelation method is the homogeneous distribution of the soluble active species from the outset of the gelation, yielding the final material: a catalyst (the silylated organometallic complex generated in situ) covalently bonded and highly dispersed on silica with a finely controlled texture. Moreover, as demonstrated in previous works [4,6,25,26], the higher reactivity of the trimethoxysilyl group compared with the triethoxysilyl group should induce the condensation of TEOS around nuclei generated by the trimethoxysilylated organometallic complexes. Palladium(II) acetate with MS–PzPy and copper(I) triflate with MS–PzPy^{Me} gave homogeneous gels with a relative mole ratio n_L/n_{TEOS} of 0.03 (Table 1). The same ratio led to a precipitate for copper(I) triflate with MS–PzPy, and it had to reach 0.08 to obtain a homogeneous gel.

After 10 days of gelation and aging at 80 °C, the solvent was slowly removed under a decreasing pressure for 90 h, and then the gels were dried for 72 h at 150 °C. At this stage, the appearance of the materials obtained was already quite different: $\text{Pd}(\text{OAc})_2(\text{SiO}_2\text{-PzPy})$ and $\text{CuOTf}(\text{SiO}_2\text{-PzPy})$ are pale brown, powdery solids a bit like talcum, and $\text{CuOTf}(\text{SiO}_2\text{-PzPy}^{\text{Me}})$ is a glassy, dark brown solid.

3.2. Textural properties

The evolution of the cumulative volume distribution over the entire pore size range for each heterogenized catalyst (Fig. 1) was obtained by the application of a combination of various methods to their respective validity domains and by adding the porous volume distributions corresponding to each domain [5,27]. The distributions of microp-

Table 2
Textural properties of dried xerogels

Sample	V_1 (cm ³ /g) ±0.01	V_2 (cm ³ /g) ±0.01	V_3 (cm ³ /g) ±0.05	V_v (cm ³ /g) ±0.1	S_{BET} (m ² /g) ±5
	<i>Micropores</i>	<i>Mesopores < 7.5 nm</i>	<i>Mesopores > 7.5 nm + macropores</i>	$V_1 + V_2 + V_3$	
Pd(OAc) ₂ (SiO ₂ -PzPy)	0.15	0.02	5.90	6.1	380
CuOTf(SiO ₂ -PzPy)	0.02	0.01	2.80	2.8	55
CuOTf(SiO ₂ -PzPy ^{Me})	0.10	0.04	1.80	1.9	290

V_1 , microporous volume obtained by the Brunauer method; V_2 , cumulative porous volume obtained following the Broekhoff–de Boer theory; V_3 , specific porous volume measured by mercury porosimetry (Washburn and Pirard's models); V_v , total cumulative porous volume; S_{BET} , specific surface area obtained by the BET method.

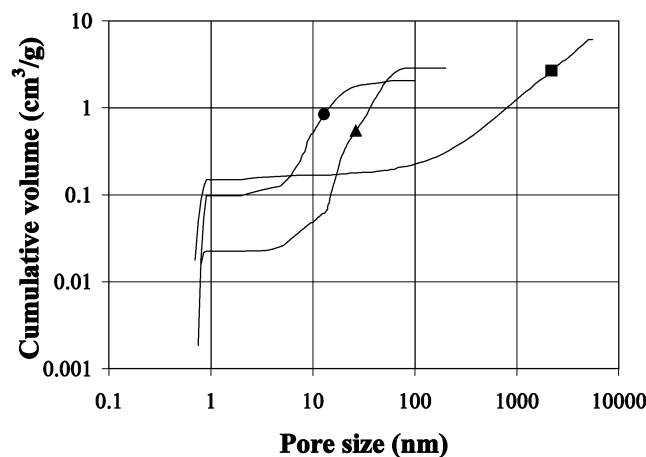


Fig. 1. Pore size distribution of samples Pd(OAc)₂(SiO₂-PzPy) (■), CuOTf(SiO₂-PzPy) (▲), and CuOTf(SiO₂-PzPy^{Me}) (●).

ores (width < 2 nm) were calculated by Brunauer's method applied to the *t*-plot derived from nitrogen adsorption isotherms [28]. The distributions of mesopores smaller than 7.5 nm were obtained by the Broekhoff–de Boer method based on nitrogen capillary condensation [28]. Mesopores larger than 7.5 nm and macropores were examined by mercury porosimetry measurements with the application of Pirard's model [27,29] and Washburn's model [28]. The total cumulative volume, V_v (Table 2), was obtained by the addition of the specific pore volume obtained by each method.

All samples are characterized by a steep volume increase around 0.8 nm, followed by a plateau. In the range of meso- and macropores, all samples exhibit a broad distribution. Accordingly, these samples then contain micropores (width < 2 nm), mesopores (2 nm < width < 50 nm), and macropores (width > 50 nm). Compared with the other two samples, the CuOTf(SiO₂-PzPy) sample exhibited the lowest specific surface area, S_{BET} , and the lowest microporous volume, V_1 (Table 2).

TEM micrograph analysis (Figs. 2a–c) shows that calcination and reduction steps produce metallic nanoparticles, the size range of which is between 2 and 5 nm. The nanoparticles are highly and homogeneously dispersed in the silica matrix, which suggests that the catalytic species from the noncalcined samples tested in cyclopropanation and in etherification are also highly dispersed and encapsulated in the silica particles. In Fig. 2c, it can be observed that copper

nanoparticles are located inside elementary silica particles, the size range of which is between 10 and 15 nm. It is more difficult to discern silica particles in Figs. 2a–b, probably because the tangle of silica particles is very important.

The above results confirm and illustrate how subtle variations of the ligand structure [compare CuOTf(SiO₂-PzPy) and CuOTf(SiO₂-PzPy^{Me})] induce major variations in xerogel texture, such as the size of elementary silica particles, pore size distribution, porous volume, and specific surface area.

3.3. Catalytic tests

3.3.1. Homogeneous catalysts

Ethyl diazoacetate (EDA) was added within 3 h to the homogeneous solution, and the progress of the reaction was followed by measurement of the volume of nitrogen evolved. The resulting solution was analyzed by GC after consumption of EDA. Tables 3 and 4 summarize the results obtained with styrene and cyclooctene, respectively. Nitrogen evolution as a function of time for the same cyclopropanation reactions is reported in Figs. 3a and 4.

It follows that palladium(II)- and copper(I)-based complexes show high catalytic activity for styrene cyclopropanation (Table 3) and for cyclooctene cyclopropanation (Table 4) in homogeneous solution at 60 °C. The only reaction products are then cyclopropane carboxylates, and only trace amounts of carbene dimers, maleate or fumarate, are detected. Although a slightly lower activity is observed with CuOTf(MS-PzPy) in cyclooctene cyclopropanation, metal coordination to either MS-PzPy or MS-PzPy^{Me} ligand does not influence the performances of homogeneous catalysts much at 60 °C. A significant loss of catalyst activity occurs at room temperature, however.

3.3.2. Heterogeneous catalysts

The corresponding immobilized organometallic complexes Pd(OAc)₂(SiO₂-PzPy), CuOTf(SiO₂-PzPy), and CuOTf(SiO₂-PzPy^{Me}) were tested under similar reaction conditions for styrene (Table 3) and cyclooctene cyclopropanation (Table 4) at 60 °C, but with a slower addition of EDA (duration of the addition of 6 h instead of 3 h, to allow the diffusion of reactants to active catalytic sites).

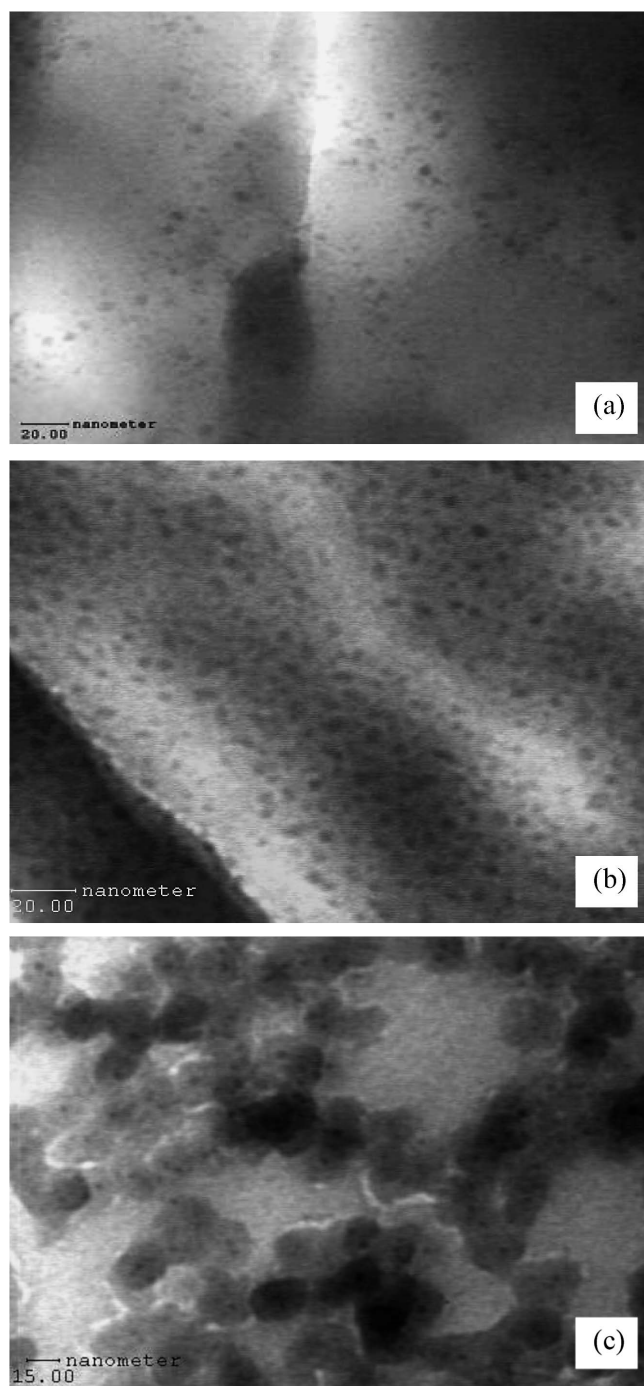


Fig. 2. TEM micrographs of Pd⁰/SiO₂ xerogel prepared from Pd(OAc)₂(SiO₂-PzPy) (350,000×) (a), and Cu⁰/SiO₂ xerogels prepared from CuOTf(SiO₂-PzPy) (500,000×) (b) and CuOTf(SiO₂-PzPy^{Me}) (350,000×) (c).

In the case of styrene cyclopropanation (Fig. 3b), the hybrid palladium-based catalysts appeared to be significantly less active than the corresponding copper-based ones. The hybrid copper-based catalysts gave good to excellent yields of styrene cyclopropane carboxylates, the yields of which are close or equivalent to those obtained in homogeneous solution, whereas a clear-cut difference was observed for

Table 3
Styrene cyclopropanation at 60 °C

Sample	V _{N₂} (%) ±2	V _{N₂} ^{fin} (%) ±2	t ^{fin} (h)	Yield (%) ±2	cis/trans ±0.02
Pd(OAc) ₂ (MS-PzPy)	78	100	< 1	98	0.54
Pd(OAc) ₂ (MS-PzPy ^{Me})	92	100	< 1	98	0.54
CuOTf(MS-PzPy)	96	100	< 1	96	0.50
CuOTf(MS-PzPy ^{Me})	98	100	< 1	96	0.78
Pd(OAc) ₂ (SiO ₂ -PzPy)	30	80	16	76	0.52
CuOTf(SiO ₂ -PzPy)	64	84	16	84	0.58
CuOTf(SiO ₂ -PzPy ^{Me})	72	96	< 1	96	0.88

EDA/M = 220, where M is either copper(I) or palladium(II); V_{N₂}, amount of N₂ evolved (% relative to EDA) after 3 h (homogeneous catalysts) or after 6 h (heterogenized catalysts); V_{N₂}^{fin}, total amount of N₂ evolved (% relative to EDA) after N₂ evolution has come to an end; t^{fin}, period of time between the end of the EDA addition and N₂ evolution has ended; Yield, yield of the reaction determined by GC; cis/trans, molar ratio of cis and trans isomers determined by GC.

Table 4
Cyclooctene cyclopropanation at 60 °C

Sample	V _{N₂} (%) ±2	V _{N₂} ^{fin} (%) ±2	t ^{fin} (h)	Yield (%) ±2	endo/exo ±0.02
CuOTf(MS-PzPy)	98	100	< 1	92	0.48
CuOTf(MS-PzPy ^{Me})	92	100	< 1	98	0.36
CuOTf(SiO ₂ -PzPy)	8	76	12	72	0.52
CuOTf(SiO ₂ -PzPy ^{Me})	86	98	< 1	96	0.46

V_{N₂}, V_{N₂}^{fin}, t^{fin}, Yield, endo/exo, see Table 3.

the two copper-based catalysts with cyclooctene. Indeed, for cyclooctene cyclopropanation under heterogeneous conditions (Fig. 4), a very good activity for EDA decomposition was observed with CuOTf(SiO₂-PzPy^{Me}), whereas a drastic loss of activity occurred with CuOTf(SiO₂-PzPy) and not all EDA was decomposed, even after 12 h in that particular case. These observations confirm that a relationship can be drawn between the kinetics of EDA decomposition and the activity for cyclopropanation, since almost no by-products, such as carbene dimers, are formed with the most active catalysts.

The stereoselectivities of the cyclopropanation reactions remain modest. The trans isomer is always preferentially obtained with styrene, the exo one with cyclooctene. The relative proportion of cis isomers is constantly higher with the PzPy^{Me} ligand, and especially so in the heterogeneous phase, which might reflect to some extent the steric constraint of the ligand and of the support.

Blank experiments with the heterogenized free ligand SiO₂-PzPy (no metal added, Fig. 3b) showed that the support does not promote decomposition of the diazocompound to a significant extent. Furthermore, the immobilized CuOTf(SiO₂-PzPy^{Me}) used for styrene cyclopropanation was recycled, and after four runs, only a slight loss of activity (about 3%) was observed, but without modification of the selectivity.

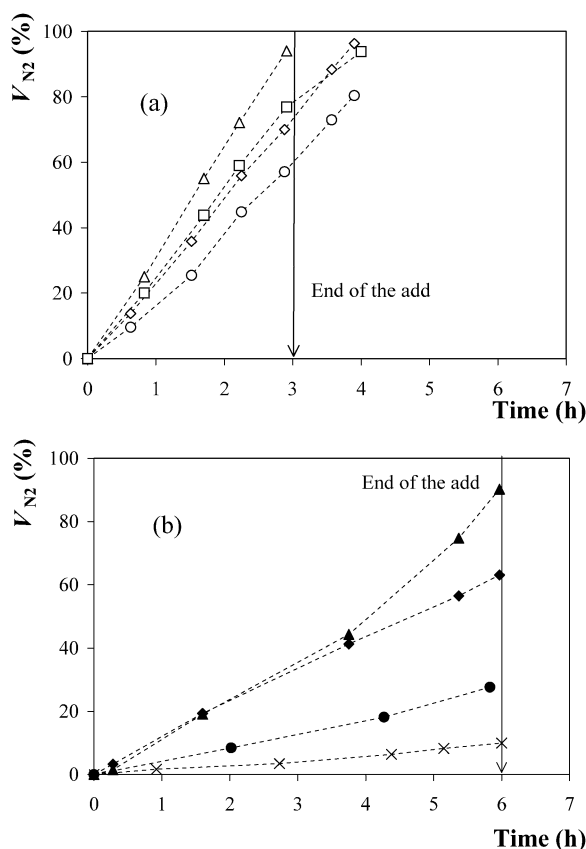


Fig. 3. Styrene cyclopropanation at 60 °C. Evolution of N₂ volume vs. time (a) with homogenous catalysts: Pd(OAc)₂(MS–PzPy) (○), Pd(OAc)₂(MS–PzPy^{Me}) (□), CuOTf(MS–PzPy) (◇), and CuOTf(MS–PzPy^{Me}) (Δ); and (b) with heterogenized catalysts: Pd(OAc)₂(SiO₂–PzPy) (●), CuOTf(SiO₂–PzPy) (◆), CuOTf(SiO₂–PzPy^{Me}) (▲), and blank experiments (×).

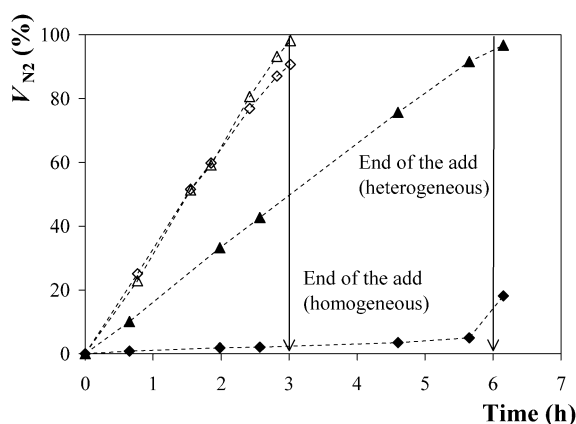


Fig. 4. Cyclooctene cyclopropanation at 60 °C. Evolution of N₂ volume vs. time with homogeneous catalysts: CuOTf(MS–PzPy) (◇) and CuOTf(MS–PzPy^{Me}) (Δ); and heterogenized catalysts: CuOTf(SiO₂–PzPy) (◆) and CuOTf(SiO₂–PzPy^{Me}) (▲).

Both homogeneous and immobilized copper-based catalysts were also tested for the chemoselectivity of carbene reactions with two unsaturated alcohols, allyl alcohol and ω -undecylenyl alcohol, respectively (Fig. 5). In both cases,

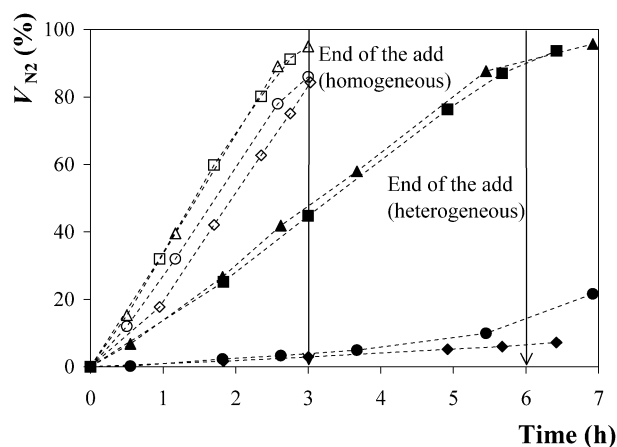


Fig. 5. O–H insertion in alcohols at 60 °C. Evolution of N₂ volume vs. time with homogeneous catalysts: CuOTf(MS–PzPy) (◇, allylic alcohol; ○, ω -undecylenyl alcohol) and CuOTf(MS–PzPy^{Me}) (□, allylic alcohol; Δ, ω -undecylenyl alcohol); and heterogenized catalysts: CuOTf(SiO₂–PzPy) (◆, allylic alcohol; ●, ω -undecylenyl alcohol) and CuOTf(SiO₂–PzPy^{Me}) (■, allylic alcohol; ▲, ω -undecylenyl alcohol).

Table 5
O–H insertion in allylic alcohol at 60 °C

Sample	V _{N₂} (%) ±2	V _{N₂} ^{fin} (%) ±2	t ^{fin} (h)	Yield (%) ±2
CuOTf(MS–PzPy)	84	96	< 1	92
CuOTf(MS–PzPy ^{Me})	100	100	< 1	94
CuOTf(SiO ₂ –PzPy)	8	20	16	18
CuOTf(SiO ₂ –PzPy ^{Me})	94	96	< 1	90

V_{N₂}, V_{N₂}^{fin}, t^{fin}, Yield, see Table 3.

either a carbene addition to the double bond or an insertion into the hydroxylic bond can take place. The double bond is next to the more polar hydroxylic group in the first example and far from it in the second one, which could influence the outcome of the competitive reactions. Homogeneous CuOTf(MS–PzPy) and CuOTf(MS–PzPy^{Me}) catalysts displayed remarkable chemoselectivity and gave high yields of –OH insertion products with both allyl alcohol and ω -undecylenyl alcohol at 60 °C (Tables 5 and 6). No formation of cyclopropane was observed. Under heterogeneous conditions, CuOTf(SiO₂–PzPy^{Me}) exhibited an activity and selectivity quite similar to those of the corresponding homogeneous catalyst at 60 °C (Tables 5 and 6). In contrast, CuOTf(SiO₂–PzPy) proved to be much less active, as was already observed for the cyclopropanation reactions. Here also, the heterogenized CuOTf(SiO₂–PzPy^{Me}) sample lost its activity at room temperature.

It thus appears that the pyrazolopyridine ligands form with copper(I) very active catalysts for cyclopropanation and for chemoselective insertion into –OH bonds of alkenols at 60 °C. If the nature of the two pyrazolopyridine ligands tested in this study (which differ by only one methyl group in position 6 of the pyridine ring) only slightly affects the activity–selectivity pattern of the reaction under homogeneous conditions, the situation is quite different with het-

Table 6
O–H insertion in ω -undecylenyl alcohol at 60 °C

Sample	V_{N_2} (%) ± 2	$V_{N_2}^{\text{fin}}$ (%) ± 2	t^{fin} (h)	Yield (%) ± 2
CuOTf(MS–PzPy)	96	98	< 1	96
CuOTf(MS–PzPy ^{Me})	94	100	< 1	96
CuOTf(SiO ₂ –PzPy)	16	20	16	22
CuOTf(SiO ₂ –PzPy ^{Me})	94	96	< 1	92

V_{N_2} , $V_{N_2}^{\text{fin}}$, t^{fin} , Yield, see Table 3.

erogenized catalysts for both the cyclopropanation reactions and the O–H insertion reactions. The different catalyst efficiencies probably result from the relatively different accessibilities of the reactants to the active sites and, in fine, from the spatial volume of the organic ligand, which determines (at least in part) the issue of the gelation process. The reactivity and selectivity of the most active xerogel-heterogenized catalysts do not deviate much from that obtained with the corresponding homogeneous complexes, though they could be used without significant loss of cyclopropanation activity and metal leaching, at least in four successive runs. A similar observation has also been reported for cyclopropanation reactions catalyzed by homogeneous and heterogenized copper and rhodium complexes on a modified USY-zeolite [30].

4. Conclusions

Previous studies have demonstrated that trimethoxysilylated organometallic complexes can act, in a sol–gel process, as nucleation agents for the gelation of TEOS in basic aqueous medium, and, consequently, the active site is located inside microporous silica particles. It had also been shown that the structure of the silyl-tethered chelating group (especially its steric hindrance) influences considerably the microstructure of the material and allows a fine control of its texture.

We report now on the first use of the pyrazolopyridine ligand for the synthesis of immobilized homogeneous catalysts. The present work demonstrates the possibility of chemisorption of a variety of homogeneous catalysts on silica by the same method as that previously reported, that is, by cogelation of trimethoxysilylated pyrazolopyridine-based organometallic complexes and TEOS in ethanolic medium in the presence of an aqueous ammonia solution. The pyrazolopyridine derivatives proved to be efficient ligands for the heterogenization of palladium and copper complexes on silica via a sol–gel process, yielding highly dispersed homogeneous catalysts covalently bonded to silica with a finely controlled structure. The textural properties of the support, such as pore volume, pore size, and surface area, are considerably influenced by the nature of the complex and can be tailored by a change in the structure of the ligand, such as MS–PzPy or MS–PzPy^{Me}. These new examples confirm and extend the results already reported in [9] for silylated acetylacetonate ligands. Further-

more, a comparison of the homogeneous with the heterogeneous catalysts shows that the textural properties of heterogenized catalysts strongly influence their catalytic activity. Indeed, the immobilized complex CuOTf(SiO₂–PzPy) is a very poor catalyst for cyclopropanation and for O–H insertion when compared with CuOTf(SiO₂–PzPy^{Me}). This probably results from favorable textural properties of the sample CuOTf(SiO₂–PzPy^{Me}), which has a higher specific surface. Although the homogeneous pyrazolopyridine-based organometallic complexes tested here display almost the same excellent catalytic activity in both olefin cyclopropanation and alcohol etherification, their corresponding heterogenized complexes via the sol-process display quite different activities. The different catalyst efficiencies probably result from the relatively different accessibilities of the reactants to the active sites and, in fine, from the spatial volume of the organic ligand, which determines, at least in part, the issue of the gelation process.

The MS–PzPy and MS–PzPy^{Me} ligands appear to be good candidates for the heterogenization of recyclable homogeneous catalysts by the sol–gel process.

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