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Study of the accessibility of phosphorus centres incorporated within ordered mesoporous organic–inorganic hybrid materials

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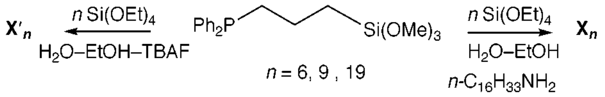
Phosphorus centres incorporated within surfactant-directed mesoporous hybrid materials are shown to be more easily accessible than those incorporated within the corresponding materials prepared in the absence of surfactant.

The one step preparation of organically functionalised ordered mesoporous silica by using non-ionic[1,3] and ionic surfactants[4–9] as structure-directing agents constitutes a new and very promising route to hybrid materials with organised functionalities. Our contribution in this field was the preparation of surfactant-directed mesoporous hybrid materials incorporating phosphino groups.[3] We showed that such materials are easily accessible and undergo further chemical reactions at phosphorus (sulfuration and quaternization) without disrupting the ordered structure and without changing notably the textural characteristics, thus suggesting the location of the P centres within the mesopore channels.[5] The potential applications of these materials containing P centres for catalysis[10] and separation which are strongly connected with the chemical accessibility of the functionalities have led us to further studies. Here, we show that, in surfactant-directed mesoporous hybrid materials, phosphorus centres are more easily accessible than in the corresponding materials prepared in the absence of surfactants.

The hybrid materials $\mathbf{X}_n$ and $\mathbf{X'}_n$ were obtained by co-hydrolysis and polycondensation of mixtures $Ph_2P(CH_2)_3Si(OMe)_3/n Si(OEt)_4$ (n = 6, 9 and 19) in the presence of *n*-hexadecylamine as template for $\mathbf{X}_n$ and in the absence of template but in the presence of 1% TBAF as catalyst for $\mathbf{X'}_n$ (Scheme 1). The molar composition of each mixture was: $1 - x$ $Si(OEt)_4$:$x Ph_2P(CH_2)_3Si(OMe)_3$: 0.27 *n*-hexadecylamine : 24.2 H_2O : 9.1 EtOH. The xerogels were prepared according to previously published procedures[3] and some relevant physical properties are given in Table 1. The BET surface areas were determined by N_2 adsorption–desorption isotherm measurements. $\mathbf{X}_n$ (n = 6, 9, 19) exhibit type IV isotherms,[11] characteristic for mesoporous materials. In contrast, the isotherms of $\mathbf{X'}_n$ are indicative of macroporosity.[11] XRD patterns for $\mathbf{X}_n$ exhibit a single diffraction peak corresponding to d_{100} spacing while no peak was observed for $\mathbf{X'}_n$. Organic incorporation was calculated by thermogravimetric analysis. It is worth noting that the calculated values are slightly closer to theoretical values for the mesoporous xerogels than for the others and this, in particular for high 'dilutions' of the organic moiety in silica. Another interesting observation in relation to the effect of dilution was made from the ^{31}P NMR data of the materials. As shown in Fig. 1, the ^{31}P NMR spectra for $\mathbf{X'}_n$ displayed signals which are always broader than those for $\mathbf{X}_n$. This is an indication of a greater mobility for the P centres in $\mathbf{X}_n$ than in $\mathbf{X'}_n$. Furthermore, on going from the 'dilution' n = 9 to the higher 'dilution' n = 19, the $Dn_{1/2}$ values remain stable for the ordered hybrid materials while for the others $\mathbf{X'}_n$, they regularly decrease as the 'dilution' increases. Thus it can be concluded that from n = 9 all the P centres within $\mathbf{X}_n$ have the same surroundings, the organic pendants being regularly dispersed at the surface of the mesopores while for the solids $\mathbf{X'}_n$ the distribution of the organic groups is random.



Scheme 1

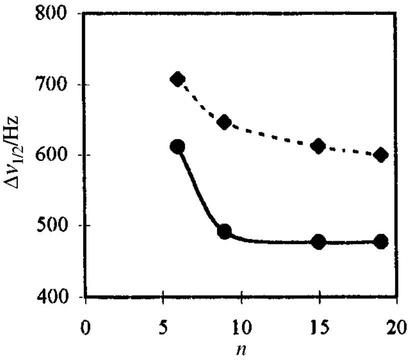


Fig. 1 Half linewidth ($\Delta\nu_{1/2}$) of the solid state ^{31}P NMR signals for $\mathbf{X}_n$ (———) and $\mathbf{X'}_n$ (-----) as a function of the 'dilution' n.

The accessibility of the P centres in these materials was investigated by using the reactions of quaternization and complexation of phosphorus centres. All the reactions at phosphorus were monitored by solid state ^{31}P NMR spectroscopy which is a reliable and sensitive probe for immobilized phosphorus groups.[12]

The solids $\mathbf{X}_n$ (n = 6, 9, 19) were treated with 1 equiv. of benzyl bromide **1** or 0.5 equiv. of α,α′-dibromoparaxylene **2** per P centre in CH_2Cl_2 at 20 °C. It is to be noted that after treatment, the ^{31}P NMR spectra of materials exhibited no signal corre-

Table 1 Physical characteristics for $\mathbf{X}_n$ ($\mathbf{X'}_n$)

Xerogel	d_{100} Lattice spacing/Å	BET surface area/m^2 g^{-1}	Total pore volume/cm^3 g^{-1}	Pore diameter[a]/Å	^{31}P CP MAS NMR (δ)	Organic incorporation[b] (%)	
$\mathbf{X_6}$ ($\mathbf{X'_6}$)	41.86 (—)	385 (149)	0.30 (—)	27 (≈300)	−15.84	14.2[c]	11 (10)
$\mathbf{X_9}$ ($\mathbf{X'_9}$)	34.41 (—)	1100 (350)	0.53 (—)	35 (≈300)	−15.71 (−15.61)	10[c]	9.4 (8.8)
$\mathbf{X_{19}}$ ($\mathbf{X'_{19}}$)	38.91 (—)	1380 (640)	0.61 (—)	34 (≈300)	−15.13 (−15.0)	5[c]	5 (4.7)

[a] Measured using the Horvath–Kawazoe pore size distribution model. [b] Percentage of Si atoms present as organosilane with respect to total Si content calculated by thermogravimetric analysis. [c] Theoretical values.

Table 2 Percentage of quaternization of P centres within $\mathbf{X}_n$ treated with **1** or (**2**) as reagent

Reaction time/h	$\mathbf{X}_6$	$\mathbf{X}_9$	$\mathbf{X}_{19}$
2	48 (35)	56 (58)	78 (74)
16	63 (68)	72 (82)	95 (90)
72	83 (83)	100 (93)	100 (100)

Table 3 Percentage of quaternization of P centres within $\mathbf{X}_n$ and $\mathbf{X'}_n$ after treatment for 24 h at 20 °C with **1** or (**2**) as reagent

n	6	9	19
$\mathbf{X}_n$	71 (73)	87 (92)	94 (95)
$\mathbf{X'}_n$	60 (72)	64 (82)	79 (70)

sponding to the oxidation of the P centres. The results given in Table 2 show that the percentage of quaternization of P centres increase with the dilution of the organic moieties in silica with both reagents. The reaction is quantitative with **1** after 72 h from $\mathbf{X}_9$ and $\mathbf{X}_{19}$. It is also quantitative with the bifunctional compound **2** from $\mathbf{X}_{19}$ after 72 h and almost quantitative from $\mathbf{X}_9$ which is noteworthy as in that case all the P centres are bridged. The same reactions were carried out on $\mathbf{X'}_n$ and the percentage of quaternization was calculated after 24 h of reaction. These results are compared to those obtained from $\mathbf{X}_n$ after the same reaction time in Table 3. It appears that the percentage of reaction with **1** is always lower from $\mathbf{X'}_n$ than from $\mathbf{X}_n$, whatever the dilution. Thus the P centres are more easily accessible within ordered mesoporous materials $\mathbf{X}_n$ than within the amorphous $\mathbf{X'}_n$. Interestingly, with the bifunctional reagent **2**, the gap between the percentage of quaternization of P centres obtained from $\mathbf{X}_n$ and $\mathbf{X'}_n$ increases with the dilution in favour of the ordered materials $\mathbf{X}_n$. This result is due to the regular distribution of organic moieties in $\mathbf{X}_n$. Indeed, while the substitution of the second bromide of **2** is promoted by the dilution within $\mathbf{X}_n$, it is rendered difficult within $\mathbf{X'}_n$ because of the random distribution of the organic groups in silica. The distribution of the organic moieties within the solids was further studied by treating the materials with 0.5 equiv. *cis*-$(PPh_3)_2PdCl_2$ per P centre. We observed that the solid state ^{31}P NMR spectra of the materials after 24 h of reaction at 20 °C in CH_2Cl_2 displayed a resonance at δ −16 corresponding to the remaining starting phosphine and a resonance at δ +16 which was assigned to the *trans* anchored phosphine Pd^{II} complex.[12] A further resonance at δ +36 was attributed to starting phosphine oxidation, which never exceeded 15%. Treatment of the materials with a large excess of the nucleophile $PBu^n{}_3$ allowed the complete elimination of the palladium liberating the starting phosphine (δ −16). The presence of the unchanged signal at δ +36 after this treatment confirmed the oxidation of the starting phosphine. The extent of the anchored phosphine Pd^{II} complex obtained from $\mathbf{X}_n$ and $\mathbf{X'}_n$ determined by ^{31}P NMR spectroscopy is shown in Fig. 2. The difference between the reactivity of materials $\mathbf{X}_n$ and $\mathbf{X'}_n$ (n = 9, 19) is important. Thus the diffusion of a bulky molecule like $(PPh_3)_2PdCl_2$ through materials $\mathbf{X'}_n$ is much more difficult than through the ordered mesoporous materials $\mathbf{X}_n$. The very low extent of reaction for $\mathbf{X}_6$ compared to $\mathbf{X}_9$ and $\mathbf{X}_{19}$ should be due to steric hindrance, which implies also that P centres are mostly located within the mesopores of $\mathbf{X}_n$.

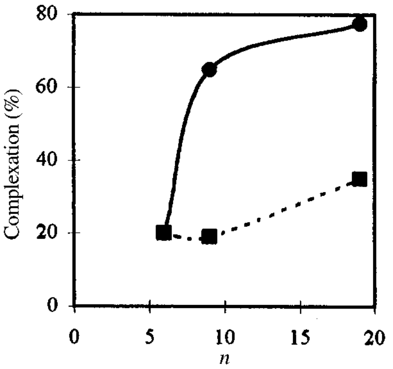


Fig. 2 Percentage of anchored phosphine Pd^{II} complex within $\mathbf{X}_n$ (———) and $\mathbf{X'}_n$ (-----).

In conclusion, we have shown that in surfactant-directed mesoporous hybrid materials, phosphorus centres are more easily accessible than in the corresponding materials prepared in the absence of surfactants. Furthermore the accessibility of phosphorus centres within ordered mesoporous hybrid materials depends on the ‘dilution’ of the organic part in silica. The higher the ‘dilution’, the greater the accessibility of the organic part in particular towards bulky reagents for which a minimum ‘dilution’ ($n > 6$) seems to be required. The study of hybrid materials with very low concentration of organo groups is in progress.

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