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ORIGINAL PAPER

Silica-supported orthophosphoric acid (OPA/SiO_2): preparation, characterization, and evaluation as green reusable catalyst for pinacolic rearrangement

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Abstract

In this paper, we report an easy-to-prepare, cost-effective, efficient, and reusable silica-supported orthophosphoric acid (OPA) catalyst for pinacolic rearrangement. The surface properties of this catalyst were successfully characterized with the help of ^{31}P NMR, TGA, DSC, FT-IR, titration, and microscopy. OPA, hydrogen bonded on the surface, is actually the active species and the reaction seems to occur in the liquid phase embedded in the silica support. As a consequence, the extracting solvent should be chosen with cautious to guarantee the recyclability of the catalyst. As example, pinacol rearrangement reactions were successfully realized with this catalyst and OPA/SiO_2 proved to be as efficient as homogeneous orthophosphoric acid to promote the reaction of pinacol derivatives. When using dichloromethane as extracting solvent, OPA/SiO_2 can be reuse up to ten times without a significant loss of activity. After ten runs, no physical damage of the catalyst has been observed by microscopy proving its suitability for such application.

Keywords Supported acid catalyst · Physico-chemical characterization · Green chemistry · Recyclability · Rearrangement

Introduction

Ortho phosphoric acid (OPA) is a well-known mineral acid which is used in fertilizers, pharmaceuticals, and detergents. It is also applied as an active homogeneous catalyst in organic synthesis. Despite the desirable catalytic activity of OPA, its separation from homogeneous reaction mixtures requires neutralization or column chromatography. To facilitate catalyst removal and minimize the amount of waste formed, OPA was immobilized onto solid supports such as SiO_2 [1–9], Nb_2O_5 [10], Al_2O_3 [11, 12], nanosilica [13], MCM-41 [14], montmorillonite [15], zeolite [16], and polysilsesquioxane [17]. Amorphous silica, which has dozens of industrial applications as an adsorbent and a filler, does not seem to have real industrial application as a catalyst, but is very largely used as a support for catalysts. This is due, among other reasons, to its good mechanical and thermal stabilities and ease of scalability [18]. Moreover, silica-supported reagents have ease of handling, low toxicity, easy separation after completion of the reaction, and reusability of the catalyst, which make them promising for both academic and industrial applications.

The combination of OPA with silica for use as a solid acid catalyst is not a new one. Initially developed in 1947 by the Shell Company for hydration of ethane [19], OPA on silica was then described in the 60th for reactions at high temperature such as aryl amination of β-naphthol [20], olefin preparation, oligomerization, and polymerization [20–23], adiponitrile preparation [24, 25], hydration of olefins to alcohols [26], or preparation of carboxylates [27]. This catalyst was recently referred as green catalyst and used in the 2000th for new applications. Among the latest, we can invoke the synthesis of bis(indolyl)alkanes [28], imino-aldol three-component couplings [29], condensation of amines and aldehydes [30], depolymerization of waster PET [31], or solvent-free cyclization of enones [32].

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The form of the silica (often a gel or diatomaceous earth), amount of OPA, and preparation method vary to meet the different acid strength requirements of the individual reactions, but an extensive period of heat treatment, generally in a calcination kiln at temperatures of 120 °C and above, tends to be a common step within each process. Condensation occurs at high temperature during calcination to give surface bridging phosphate (Si–O–P=O), diphosphorus pentaoxide (P_2O_5), and pyrophosphate groups accompanied by loss of water [33–36]. The hydrolysis process is reversible [37]. According to the literature, when the mixture of OPA/SiO_2 is dried between 100 and 200 °C, a large portion of OPA is uncombined, i.e., no phosphate bond is created. A few reports deal with the preparation and characterization of non-calcined OPA catalysts. As a part of our program toward the development of environmentally benign protocols, herein, we report such a silica-supported OPA catalyst for pinacol-pinacolone rearrangement. We have successfully characterized this silica-supported catalyst with the help of ^{31}P NMR, TGA, DSC, FT-IR, XRD, and titration.

Experimental

Materials and instruments

All commercially available products and solvents were used without further purification. Reactions were monitored by TLC (Kieselgel 60F254 aluminum sheet) with detection by UV light or potassium permanganate acidic solution. Column chromatography was performed on silica gel 40–60 µm. Flash column chromatography was performed on an automatic apparatus, using silica gel cartridges. ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on a 400 MHz/54 mm ultralong hold. Chemical shifts (δ) are quoted in parts per million (ppm) and are referenced to TMS as an internal standard. Coupling constants (J) are quoted in hertz. FT-IR spectra of the silica support, free OPA, and catalyst have been recorded using a Varian 600-IR Series spectrometer. The samples were scanned within a range of 400–4000 cm^{-1}. The thermal stability of OPA/SiO_2 was investigated by thermogravimetric analysis (TGA) using a PerkinElmer TGA 4000 apparatus and differential scanning calorimetry (DSC) using a PerkinElmer DSC 6000 apparatus coupled with an intracooler.

Preparation of the catalyst OPA/SiO_2 by wet impregnation

33 wt.% OPA/SiO_2 was prepared by adding liquid 75% OPA on a suspension of silica gel (70–200 mesh) in Et_2O. The suspension is stirred at room temperature during 1 h, and then, the solvent is removed under moderate vacuum. The resulting homogenized, white free flowing powder is stored tightly capped, studied, and used as obtained without any more drying or calcination.

General procedure for pinacolic rearrangement

In a typical procedure, pinacol **1a** (1 mmol) is simply adsorbed on 2 eq (600 mg) of catalyst and heated without stirring in an oil bath. The crude product is then extracted by dichloromethane (2*10 mL) and evaporated under vacuum. The crude mixture is then purified by flash chromatography by heptane/AcOEt if needed. The obtained products are then analysed and identified by mass spectrometry, ^{1}H, and ^{13}C NMR (see ESI).

Results and discussion

Structure of non-calcined OPA/SiO_2 catalyst

Different analytical techniques have been used to characterize the structures of surface species of OPA catalyst. The surface properties of amorphous silica, which is considered to be an oxide adsorbent, in many cases, depend on the presence of silanol functionalities [38]. The OH groups act as the centers of molecular adsorption during their specific interaction with adsorbates capable of forming a hydrogen bond with the OH groups, or, more generally, of undergoing donor–acceptor interaction [38].

Surface OH groups are subdivided as follows (Fig. 1): (1) isolated free (single silanols), SiOH; (2) geminal free (geminal silanols or silanediols), –Si$(OH)_2$; (3) vicinal, or bridged, or OH groups bond through the hydrogen bond (H-bonded single silanols, H-bonded geminals, and their H-bonded combinations). On the SiO_2 surface there also exist surface siloxane groups or Si–O–Si bridges with oxygen atoms. Moreover, there is structurally bond water inside the silica skeleton leading to internal silanol groups. When OPA is adsorbed on silica, different bonds can be observed such as hydrogen bonding with surface or core silanols (IV) or creation of bridged structures such as I, II, or III (Fig. 1). Figure 2 illustrates XRD spectra of OPA/SiO_2. The structure of the catalyst is greatly affected by OPA loading. A broad peak attributed to SiO_2 is seen around $2\theta = 22°$. The ill-defined shape of the peak proves that silica is amorphous. The pattern for the OPA/SiO_2 shows diffraction peaks that indicate the presence of some crystalline phases, although the presence of an amorphous phase is also evident. The XRD spectra of OPA/SiO_2 are different from those reported by Xie et al. for SiO_2/P_2O_5 but shares similarities with those reported by Takezawa et al. for calcined OPA/SiO_2 [39, 40]. The XRD spectra of the catalyst after three runs of reaction did not show any significant variation.

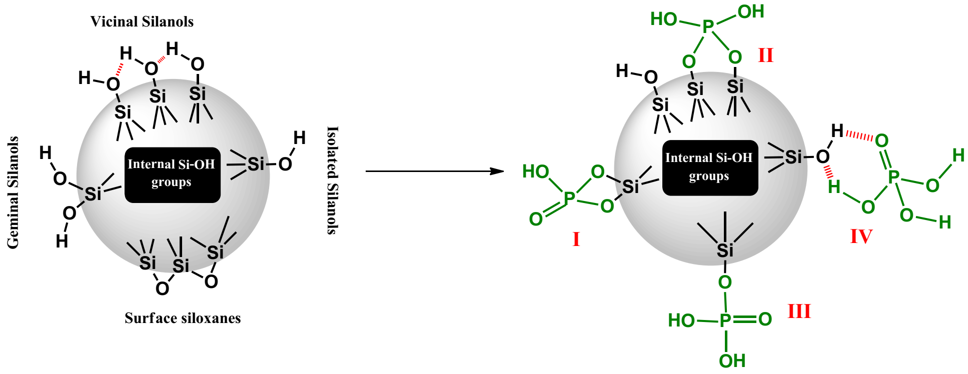


Fig. 1 Potential structures between silica and phosphoric acid [38–40]

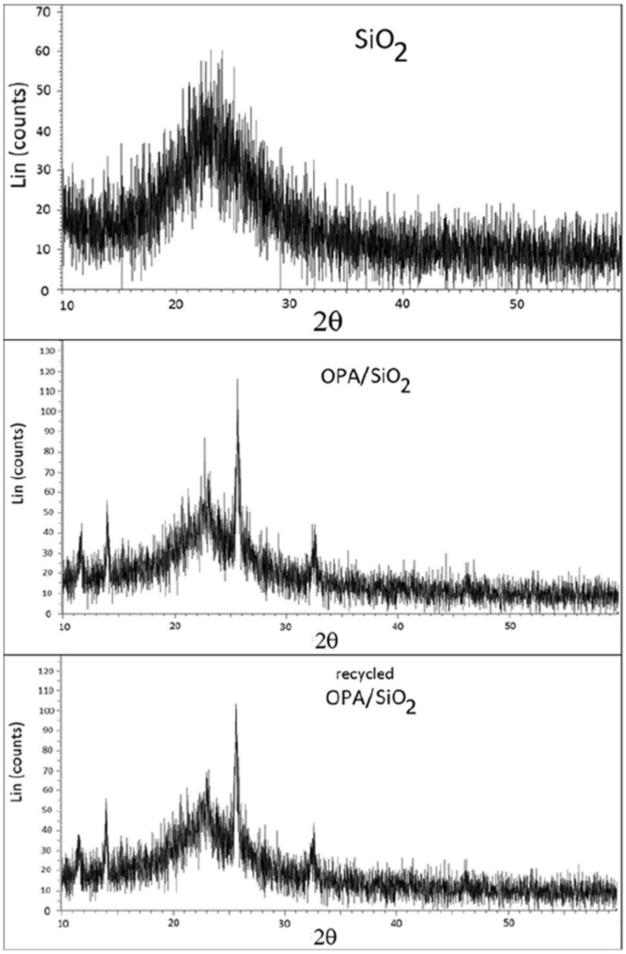


Fig. 2 XRD spectra of SiO_2, OPA/SiO_2, and OPA/SiO_2 recycled three times

Acid–base titrations were used to measure acid capacity, which is the quantity of catalytically active sites of samples. In a typical measurement, 1 g of solid was suspended in 100 mL of distilled water. The suspension was stirred between 1 and 60 min, filtered and titrated with 0.1 M NaOH in the presence of methyl orange. The release of acid is fast and progressive until 30 min of stirring. As this time, all acid has been released in water. This maximal acid-exchange capacity is well correlated with the catalyst preparation. Thus, OPA seems only adsorbed on the surface of silica gel and available for reaction as acid catalyst (Table 1 and Fig. 3).

Table 1 Titration of the acid-exchange capacity

Entry	Time of stirring (min)	Acid capacity (eq. kg^{-1})	Acid ratio on silica (w/w) %
1	1	0.8	7.8
2	3	1.1	10.8
3	5	1.5	14.7
4	10	2.1	20.6
5	20	2.8	27.4
6	30	3.2	31.4
7	45	3.2	31.4
8	60	3.2	31.4

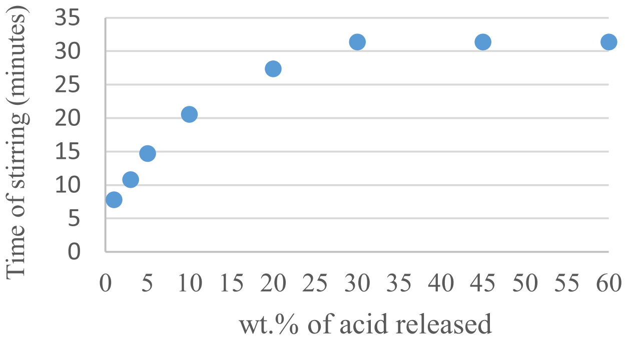


Fig. 3 Acid releasing versus time of stirring

The releasing of acid was correlated to the hydrogen-bonding capacity and polarity of various solvents. To measure this parameter, the catalyst (50 mg) was suspended in 5 mL of each solvent and stirred for 30 min. Then, the catalyst was filtered off and the solution was diluted to 50 mL by distilled water containing 5 wt.% methyl orange and titrated by 1N NaOH. Figure 4 depicted the variation of color

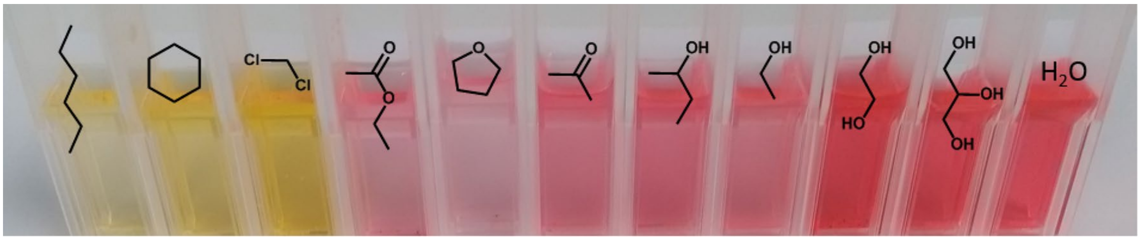


Fig. 4 Set of samples before titration in the presence of methylorange. The solution turned pink in the presence of acid

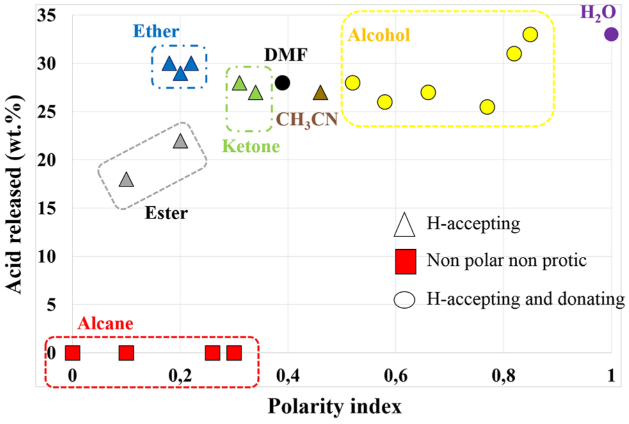


Fig. 5 Acid-exchange capacity versus polarity index of screened solvents [41]

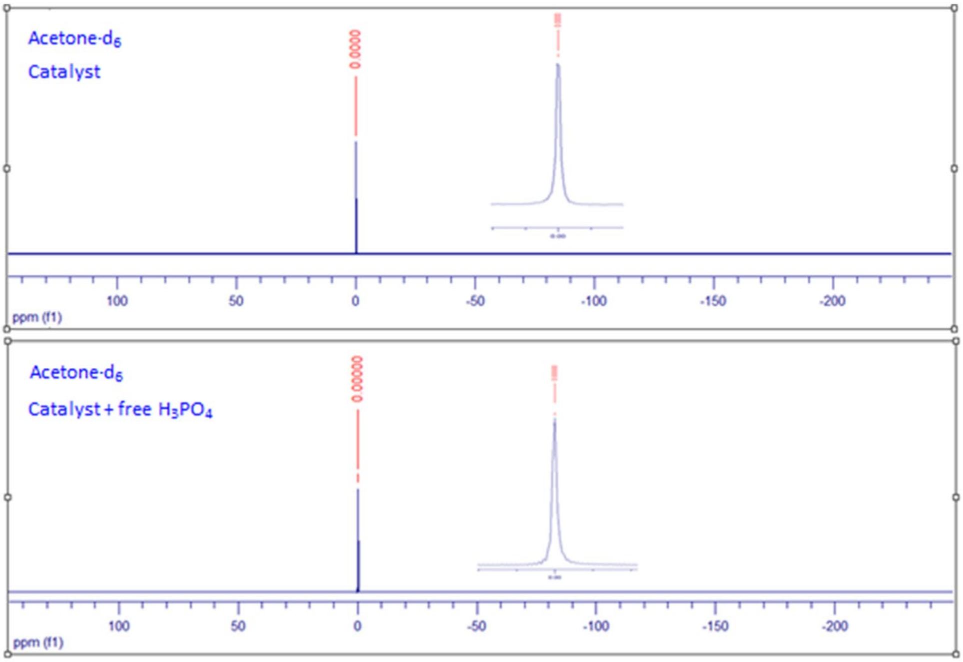
(directly correlated to acid contain) observed before titration. Basic media exhibit a yellowish color, whereas acidic media are pink-colored. As the concentrations in methylorange are similar, the color is directly correlated to the acidity of each medium. Figure 5 represents the amount of acid titrated in solution versus the polarity index of solvents [41]. 21 Solvents have been screened and assembled based on their chemical structures. The hydrogen-bonding capacity is essential for the release of acid from silica. As OPA is strongly hydrogen bonded to silica, solvent with high polarity such as alcohols is needed to extract the acid from its support. Ethers and ketones, able to create hydrogen bonds with OPA, are also good solvents to release the acid. Esters seem to be less active in releasing. Chlorinated solvents such as DCM, pure alkanes, or aromatics did not exhibit any potential to extract acid from silica. As a consequence, to avoid acid leaching during reaction and treatment, solvents like DCM, heptane, or toluene should be selected.

To identify the different labile phosphated species present in the catalyst, ^{31}P NMR studies have been realized in different solvents, adapted from the literature protocols [39, 40]. The catalyst (10 mg) is suspended in 2 mL of deuterated solvents (DMSO-d6, D_2O, $(CD_3)_2CO$, $CDCl_3$, and C_6D_6) and analysed by ^{31}P NMR without filtration. The spectra in DMSO-d6, D_2O and Acetone-d_6 were quite similar (Fig. 6). A sole peak emerged at 0 ppm for each solvent. Mixture of the suspension and liquid OPA was realized and confirmed that this sole peak is OPA. In such conditions, no spectral signals attributed to tetra-coordinated phosphorus species ($\delta_{\text{reported}} = -10$ to -40 ppm) nor pyrophosphate bond **II** ($\delta = -46$ ppm) have been observed (Fig. 6) [11, 42, 43]. No peak appeared in $CDCl_3$ or toluene and confirmed the absence of release of acid in such solvents.

To gain knowledge on the structures of surface species, FT-IR spectra of the silica support, free OPA, and catalyst have been recorded using a Varian 600-IR Series spectrometer and compared with the literature [44–58]. Data were recorded from 400 to 4000 cm^{-1}. Figure 7 displays the recorded spectra for silica (green), OPA (pink), and catalyst (dark red).

The most relevant bands are collected in Table 2. Hydrophilic, free silanols are well evident in the IR spectra by a strong band in the region with the main maximum at 3700 cm^{-1}. The acidity of these silanols is weak [46–58]. Much data suggest that almost all silanol groups absorbing at 3680–3800 cm^{-1} represent the active sites in the adsorption of both polar molecules such as water, giving rise to $\Delta H_{\text{ads}} \approx 50$ kJ/mol, because of hydrogen bonding of moderate to strong strength. The very strong and broad IR band at 1064 cm^{-1} with a shoulder at 1188 cm^{-1} is usually assigned to Si–O–Si asymmetric stretching vibrations. The IR band at 935 cm^{-1} can be assigned to silanol groups (Si–OH). The IR band at 800 cm^{-1} can be assigned to Si–O–Si symmetric-stretching vibrations, whereas the IR band at 470 cm^{-1} is due to O–Si–O-bending vibrations [46–58]. Free OPA displays a band at 1110 cm^{-1}, characteristic for symmetric P=O vibrations. The symmetric P–OH bond vibration is recorded at 876 cm^{-1} and the asymmetric P–OH vibration at 950 cm^{-1}. The P–O–H-stretching modes were observed as broad peaks at about 2280 and 2748 cm^{-1}. In H_3PO_4, the broadband between 3500 and 3600 cm^{-1} corresponds to P–OH groups which are “free” or interact only to a small extent with their environment. The band at 1625 cm^{-1} refers to OH stretch on O=P–OH bonds. The FT-IR data for the catalyst display seven bands of interest to identify the interaction between OPA and silica. First of all, no characteristic vibrational

Fig. 6 ^{31}P NMR spectra of catalyst and mixture of catalyst and free orthophosphoric acid in Aceton-d$_6$



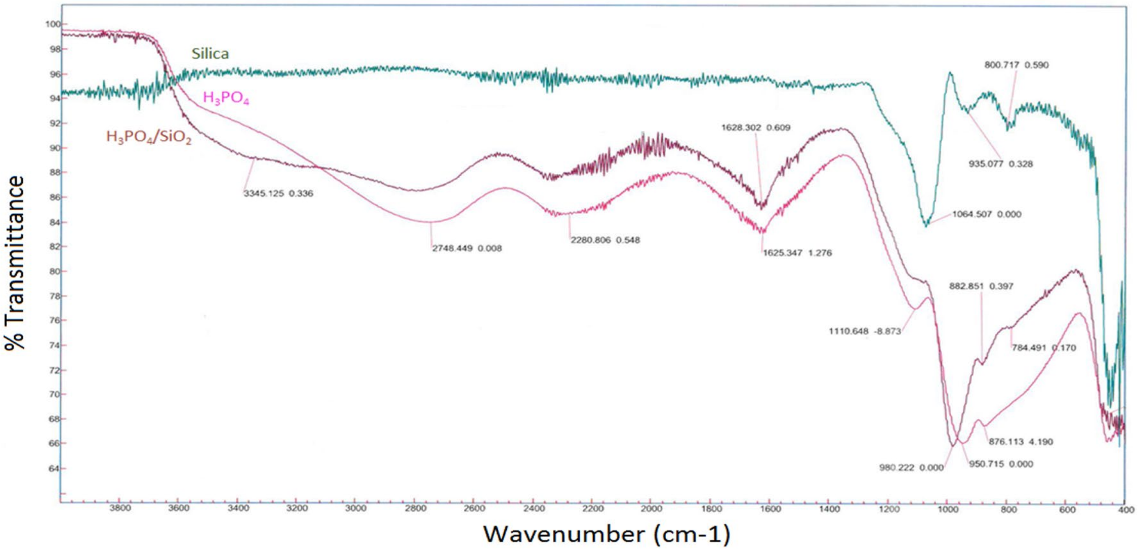


Fig. 7 Overlay of IR spectra for silica gel (green), OPA/SiO$_2$ (dark red), and free OPA (pink)

Table 2 Main bands observed

OPA/SiO$_2$ [cm^{-1}]	OPA [cm^{-1}]		SiO$_2$ [cm^{-1}]	
784	876	P–OH	470	O–Si–O
883	950	P–OH	800	Si–O–Si
1112	1110	P=O	935	Si–OH
1628	1625	O=P–**OH**	1064	Si–O–Si
2300	2280	P–O–H	1188	Si–O–Si
2600–3000	2748	P–O–H	3800 – 3600	Si–OH and H_2O
3200–3700	3500–3600	Free P–OH		

features of the –Si–O–P and –Si–O–P=O have not been observed (reported respectively at 1020 and 1320 cm^{-1}) [59]. In OPA/SiO$_2$, P–OH groups are strongly hydrogen bonded to silanols; that is why the implicated bands are enlarged and shifted. The hydrogen bonding is also proved by the disappearance of the Si–OH band at 935 cm^{-1}. Globally, the structure of O=P(OH)$_3$ is not chemically changed, but the hydrogen bonding led to some shifts in the characteristic bands for both acid and silica.

The thermal stability of OPA/SiO$_2$ was investigated by thermogravimetric analysis (TGA) using a PerkinElmer TGA 4000 apparatus. This thermal analysis is commonly used to provide information about chemical phenomena including chemisorption, dehydration, or sublimation. In our case, the TG curve (Fig. 8, in red) showed two clearly distinct weight losses, well characterized by the derivative curve (Fig. 8, in blue). The first one can be related to desorption of water molecules from the support (Peak$_{max}$ = 101 °C). The second one is attributed to the loss of OPA (Peak$_{max}$ = 167 °C). According to TGA, the amount of water supported on silica is evaluated at 12 wt.%. From the catalyst preparation, the amount of water is expected at 11 wt.% which is well correlated with practical data. However, the amount of phosphoric acid supported on silica was evaluated to around 10 wt.%, which is far less than the amount of acid titrated (Fig. 8). As a consequence, acid–base titration of the residual powder after TGA has been performed. As expected, the amount of residual acid on the silica has been titrated at 19 ± 1 wt.%, suggesting that a large amount of OPA remained trapped onto the support.

In addition, TGA was conducted with a fresh sample to 1000 °C (Fig. 9), showing no clear additional weight loss. A slight broad peak appeared around 360 °C which could be attributed to P_20_5, potential product obtained from OPA by dehydration, which is known to sublimate at 360 °C. This experiment proved that the amount of P_20_5 is very low compared with those of OPA. From these first results, it was hypothesized than OPA is retained on the silica by strong hydrogen bonding which could be broken in the presence of water. As a consequence, a sample of fresh catalyst was submitted to TGA till 350 °C under air flow. The residue was recovered and weighted. Pure water—100% w/w—was added in the solid and suspended in diethyl ether at room temperature during 10 min. This procedure should allow OPA to be released in aqueous ether. After 10 min, diethyl ether is evaporated with caution under moderate vacuum. The residual white powder is then submitted again to TGA analysis (Fig. 10). The treatment has been useful and the addition of water helped to desorb OPA from silica. This thermogravimetric analysis proved that OPA still remained on silica after heating at 350 °C. The same treatment has been repeated a third time, showing the same behavior for the catalyst. The residual powder was titrated as a 6 wt.% OPA/SiO$_2$.

As reported in Fig. 11, the thermal behavior was completed by the DSC analysis, which also showed two distinct peaks which can be attributed to loss of water (peak 1), and then at loss of OPA (Peak$_{max}$ at 204.90 °C). Considering the amount of acid on silica, the DH for release of acid has been evaluated to DH ≈ 9 kJ.mol^{-1} which can

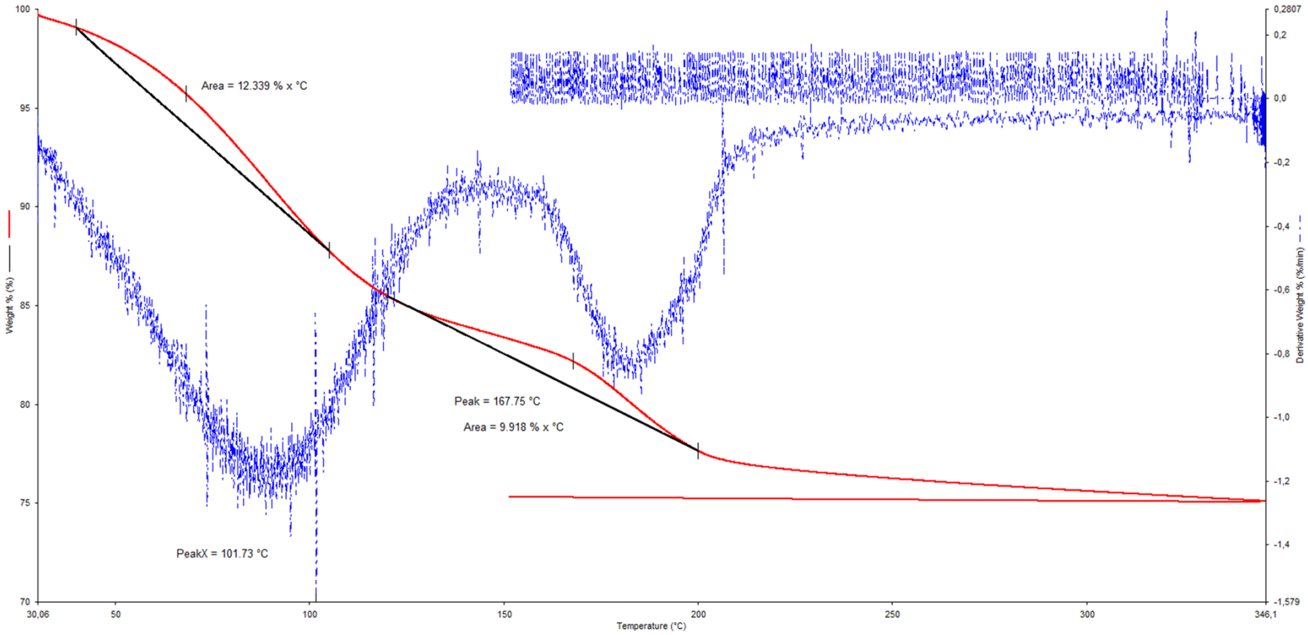


Fig. 8 TGA curve from 30 to 350 °C for catalyst OPA/SiO$_2$ (TG curve in red; derivative in blue)

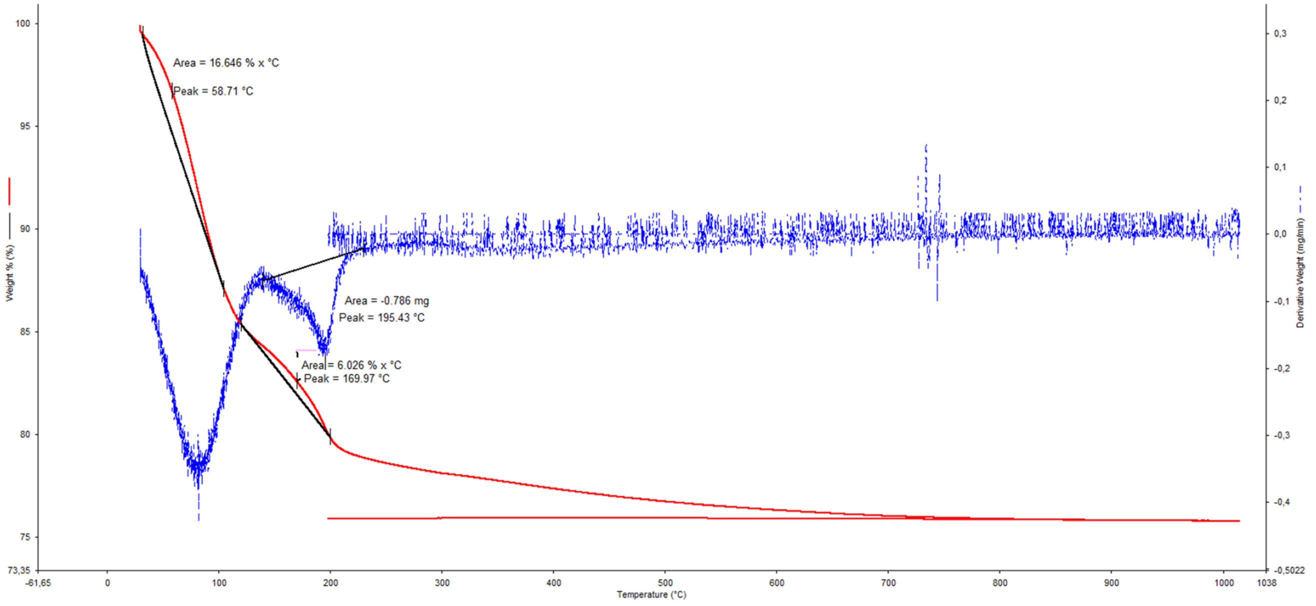


Fig. 9 TGA curve from 30 to 1000 °C under air flow (TGA curve in red; derivative curve in blue)

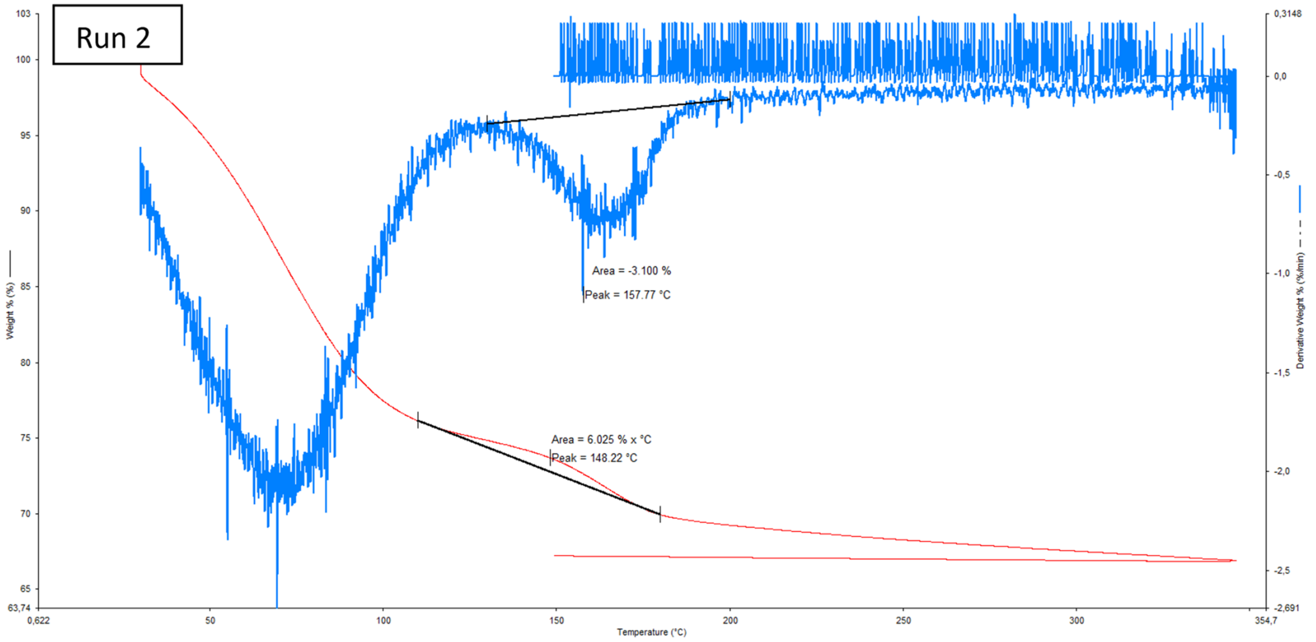


Fig. 10 TGA curves after treatments by aqueous diethyl ether

be attributed to hydrogen-bond breaking. A small peak around 360 °C could be referred as sublimation of P_2O_5. As observed in TGA, its quantity is negligible compared to those of water and OPA.

Applications: pinacolic rearrangement

As an exploratory application in organic synthesis OPA/SiO_2 was used as catalyst for the pinacolic rearrangement

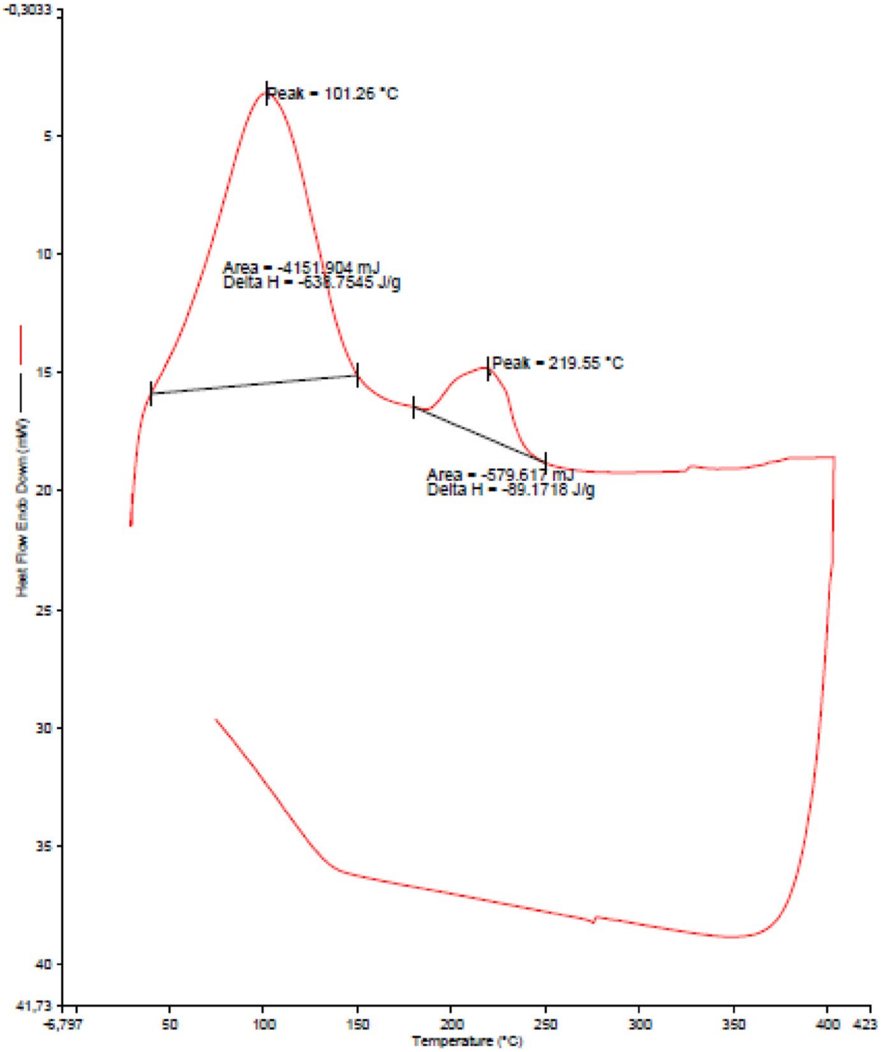
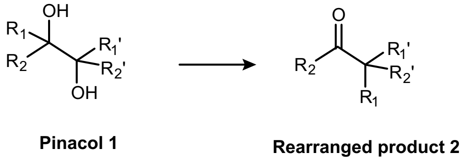


Fig. 11 DSC of the OPA/SiO_2 catalyst

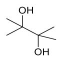
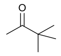
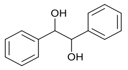
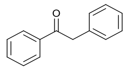
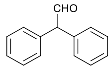
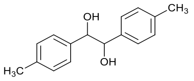
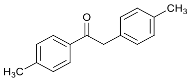
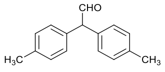
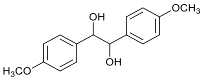
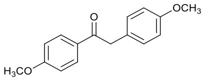
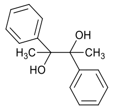
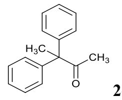


Scheme 1 Pinacolic rearrangement of pinacol derivatives **1**

of some pinacol derivatives. Pinacolic rearrangement is a transformation of particular interest, often applied for natural products synthesis (Scheme 1) [60–62]. Typically, the reaction has been reported using strong Brönsted acids such as H_2SO_4, $HClO_4$–HOAc, Cl_3CCOOH, HBr, or HI at temperature above 100 °C [63–70]. Moreover, the acidity of the medium is reported as essential to run the pinacolic rearrangement [71].

To facilitate the recovery of product and reuse the catalyst, the reaction was conducting in solvent-free conditions under the conventional heating with pinacol **1a** as substrate (Table 3). In the presence of OPA/SiO_2 (2 eq.) at 180 °C, the reaction occurred smoothly and pinacol **1a** gave a quantitative yield in 3,3-dimethylbutan-2-one (**2a**) after 30 min. Decreasing the temperature conducted to lower conversions and yields even if no side-products were observed (Table 3, entries 2–4). At 100 °C, the reaction did not occur and the starting material is recovered unchanged (Table 3, entry 4). As a comparison, silica alone did not allow any conversion, even at 180 °C (Table 3, entry 5). Using 1 equivalent of acid catalyst conducted to lower yield (Table 3, entry 6). Silica did not allow any reaction of the different substrates used (Table 3, entries 11, 17, 20 and 23). When hydrobenzoin **1b** is heated at 180 °C in the presence of 2 eq. of OPA/SiO_2, a complete conversion is observed but a mixture of products is obtained (Table 3, entry 8). 1,2-Diphenylethanone **2b** and 2,2-diphenylethanal **2b'** are obtained in a 57:43 ratio. A similar ratio of products is obtained when using two equivalents of homogeneous OPA (Table 3, entry 9). This result tends to

Table 3 Scope of the reaction

Entry	Substrate	Product	Catalyst	Amount (mg)	T(°C)	Time (min)	Conversion (%)	Yield (%)
1	 **1a**	 **2a**	OPA/SiO_2	600	180	30	100	100
2			OPA/SiO_2	600	150	30	80	80
3			OPA/SiO_2	600	120	30	20	20
4			OPA/SiO_2	600	100	30	0	-
5			SiO_2	600	180	30	0	-
6			OPA/SiO_2	300	180	30	50	50
7			OPA/SiO_2	300	180	120	80	80
8	 **1b**	 **2b**  **2b’**	OPA/SiO_2	600	180	30	100	**2b:2b’** 57:43
9			OPA	200	180	30	100	60:40
10			OPA/SiO_2	300	180	120	70	**2b:2b’** 40:60
11			OPA/SiO_2	1200	180	20	100	**2b:2b’** 70:30
12			OPA	400	180	30	100	72:28
13			SiO_2	600	180	30	0	-
14	 **1c**	 **2c**  **2c’**	OPA/SiO_2	500	180	30	100	**2c:2c’** 53:47
15			OPA/SiO_2	250	180	120	70	**2c:2c’** 42:58
16			OPA/SiO_2	1000	180	20	100	**2c:2c’** 68:32
17			OPA	335	180	30	100	65:35
18			SiO_2	500	180	30	0	-
18	 **1d**	 **2d**	OPA/SiO_2	500	180	30	100	100
19			OPA/SiO_2	250	180	120	80	80
20			OPA	335	180	30	100	75
21			SiO_2	500	180	30	0	-
22	 **1e**	 **2e**	OPA/SiO_2	500	180	30	100	100
23			OPA/SiO_2	250	180	120	50	50
24			OPA	335	180	30	100	35
25			SiO_2	500	180	30	0	-

[a] In a typical procedure, pinacol **1a** (1 mmol) is simply adsorbed on 2 eq (600 mg) of catalyst and heated without stirring in an oil bath

prove that OPA, even supported on silica, is easily available for the substrate during the reaction.

Carrying the reaction with 1 eq. of acid allowed to increase the selectivity in favor of 2,2-diphenylethanal **2b’**, but the conversion is limited to 70% after 2 h (Table 3, entry 10). On the opposite, increasing the amount of catalyst to 4 eq. conducted to a higher selectivity for 1,2-diphenylethanone **2b** (Table 3, entry 11). Comparable results are obtained with four equivalents of homogeneous OPA (Table 3, entry 12). The results tend to prove that more acidic media led to hybrid migration (to 1,2-diphenylethanone **2b**) and than a lower acidic medium led to phenyl migration (to give 2,2-diphenylethanal **2b’**). The same tendency is observed for 1,2-di-*p*-tolylethane-1,2-diol **1c** (Table 3, entries 12–18). However, when 1,2-bis(4-methoxyphenyl) ethane-1,2-diol **1d** is used a substrate, the reaction is chemoselective and led to the quantitative formation of 1,2-bis(4-methoxyphenyl)-ethanone **2d**. This selectivity could be attributed to the high mesomer electro-donating ability of the *p*-methoxy group which stabilize the intermediate of the reaction. Substrate **1e** led also to the selective production of

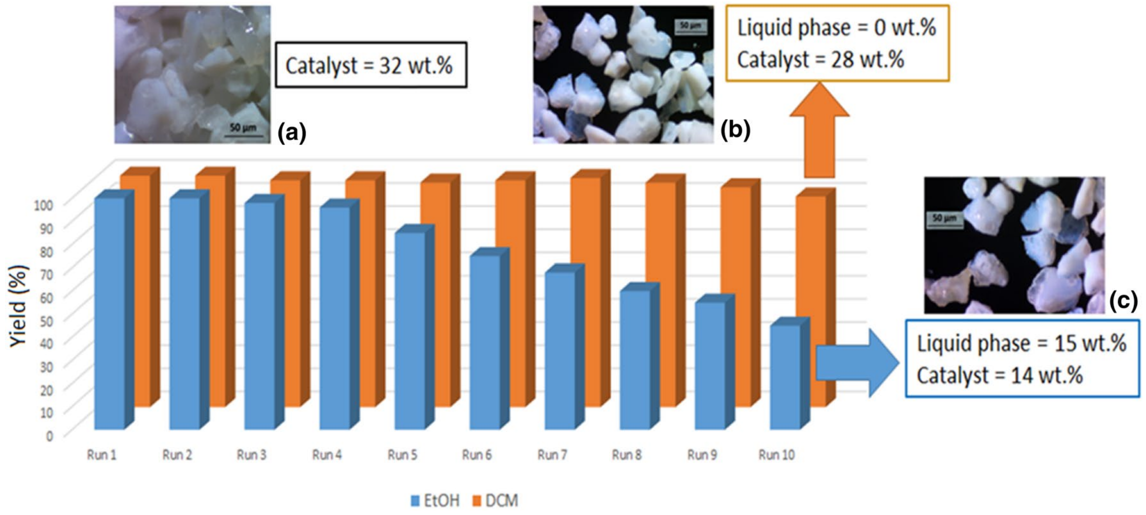


Fig. 12 Recyclability of the catalyst with DCM or EtOH as extracting solvent

3,3-diphenylbutan-2-one (**2e**), which could be attributed to a better migration ability of the phenyl group compared to the methyl group (Table 3, entries 21–23) [72, 73]. The selectivity and yield are better than those reported for strong Brönsted acid-mediated pinacolic rearrangement of **1e** [74–87].

To evaluate the recyclability of the catalyst, ten runs of reaction of pinacol **1a** were carried out. For each run, extraction of the product by a solvent was realized; the catalyst was filtered off and dried at room temperature before being engage in the next run. Dichloromethane or ethanol was used for the extraction of the product between each run. Conversion and yield were measured by HPLC, and the amount of acid was titrated in the extracting solvent and in the catalyst after ten runs (Fig. 12). As expected DCM did not led to any leaching of acid in the liquid phase during extraction. However, the solid part was titrated to 28 wt.% of acid, compared with the initial amount of 32 wt.%. This low decrease could be attributed to physical loss during filtrations. Moreover, as expected, using ethanol as extraction solvent led to a decrease in conversion during time. This is due to the leaching of acid in the liquid phase. After 10 runs, 15 wt.% of acid is titrated in the combined liquid phases and only 14 wt.% remained on the catalyst. This yield of the reaction is greatly impacted by this loss in acid. After 10 runs, the conversion only reached 45%, which is comparable with the result obtained using only one equivalent of acid (Table 3, entry 6). As a consequence, the choice of the extraction solvent is of great importance for reaction with OPA/SiO_2. According to the microscopic observations, this loss of activity is rather due to leaching of acid more than to physical damages of the support.

Conclusion

A simple and recyclable silica-supported OPA catalyst has been prepared, characterized, and used to devise a mild and efficient protocol for pinacolic rearrangement of some pinacol derivatives. This catalyst can be called green because of its ease of preparation, mildness, easy workup procedure (filtration), and its stability in air. Apart from this, the solvent-free reaction conditions and applicability to a wide spectrum of pinacol derivatives are other advantages of the present protocol. The choice of extraction solvents is of great importance to guarantee the recycling of the catalyst and, thus, the efficiency of the proposed OPA/SiO_2-catalyzed transformations.

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