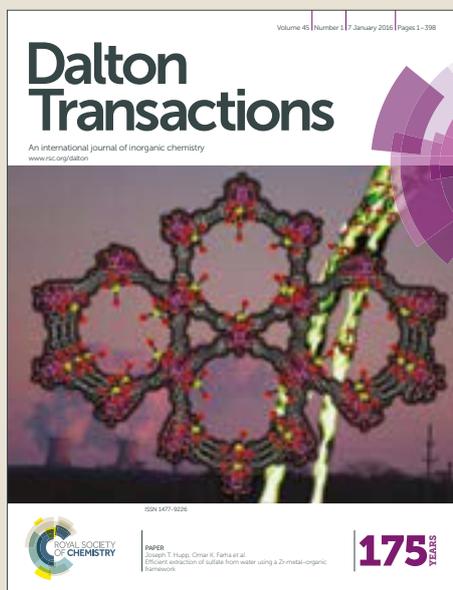


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Clean Chlorination of Silica Surfaces by a Single-site Substitution Approach

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Accepted 00th January 20xxNiladri Maity,^{a,b} Samir Barman,^a Edy Abou-Hamad,^a Valerio D'Elia,^{*a,c} and Jean-Marie Basset^{*a}

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A chlorination method for the selective substitution of well-defined isolated silanol groups of the silica surface has been developed using the catalytic Appel reaction. Spectroscopic analysis, complemented by elemental microanalysis studies, reveals that a quantitative chlorination could be achieved with highly dehydroxylated silica materials that exclusively possess non-hydrogen bonded silanol groups. The employed method did not leave any carbon or phosphorous residue on the silica surface and can be regarded as a promising tool for the future functionalization of metal oxide surfaces.

Introduction

Owing to their stability, versatility, insoluble nature in organic solvents and ubiquitous availability, silica-based materials have been widely employed as supports in catalysis.^{1, 2} On one hand, judiciously shaped and functionalized mesoporous silica materials play a crucial role in reducing the gap between homogeneous and heterogeneous catalysts.³⁻⁶ On the other hand, well-defined single site organometallic and coordination complexes supported on silica surface by the surface organometallic chemistry approach (SOMC)⁷⁻⁹ have performed as potent catalysts for a wide range of reactions, such as olefin metathesis,¹⁰⁻¹² alkane metathesis,^{13, 14} CO₂ conversion to cyclic carbonates^{15, 16} and methanol,¹⁷ oxidative dehydrogenation of propane¹⁸ and CO oxidation.¹⁹ With the surface of silica being constituted of strained siloxane bridges ($\equiv\text{Si-O-Si}\equiv$) and silanol ($\equiv\text{Si-OH}$) moieties,⁹ an additional way to exploit this material as a support in catalysis is represented by opportune modifications or replacement of these functionalities to generate new supports with different properties. Focusing exclusively on modifications where the newly introduced functional groups are directly bound to silicon atoms of the surface, controlled reaction of ammonia with the siloxane bridges of SBA-15 allowed the formation of ($\equiv\text{Si-NH}_2$) moieties acting as silylamido ligands for immobilizing catalytically relevant organometallic complexes.^{20, 21} Considering that the grafting reactions on silica surface rely

almost exclusively on the nucleophilic attack of the surface silanols to the precursor complexes,^{7, 9} a different and attractive strategy to modify the surface of silica would be by replacing the $\equiv\text{Si-OH}$ moieties with leaving groups. This transformation would potentially lead to an *umpolung*²² of the participating silicon atoms allowing them to react with metal complexes bearing nucleophilic functionalities and enabling access to new surface structures. In this context, the synthesis of chlorinated silica has been reported by various authors in the past. Kamitori et al. reported the reaction of silica gel with excess thionyl chloride (SOCl₂) and the application of the thus synthesized material as a catalyst for the thioacetalization of aldehydes.²³ Several applications of similarly prepared chlorinated silicas in organic synthesis have been subsequently reported.²⁴⁻²⁶ Khodabakhshi, Karamiet *al.* have studied the reaction of sodium tungstate (Na₂WO₄) with chlorinated silica.^{27, 28} It has been proposed that the reaction of the $\equiv\text{Si-Cl}$ surface moieties with Na₂WO₄ generates $\equiv\text{Si-O-WO}_3\text{Na}$ sites by nucleophilic substitution of the chloride anions. Following protonation of the supported tungstate with aqueous HCl, the ensuing supported tungstic acid could be employed as a catalyst for several organic condensations.²⁷⁻³¹ These advances highlight the potential importance of chlorinated silica as a catalyst and a support, however, the chlorination of the silica surface has not been studied in detail. It is not known whether the chlorination reaction involves the silanol moieties and/or the siloxane bridges. The efficiency of chlorination with respect to the nature of the silica support (i.e. density and degree of isolation of the surface silanols) has, to the best of our knowledge, not been investigated in detail. Furthermore, the development of more controlled and atom-economic procedures than the use of excess SOCl₂ would be desirable. Therefore, we report here a study on the accurate and selective transformation of the isolated $\equiv\text{Si-OH}$ groups by $\equiv\text{Si-Cl}$ surface functionalities on different kinds of dehydroxylated silica surfaces (SiO₂₍₇₀₀₎, SiO₂₍₅₀₀₎ and SiO₂₍₂₀₀₎) being respectively

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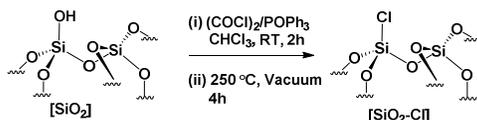
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† Electronic Supplementary Information (ESI) available: Microanalysis data of the prepared compounds, IR spectrum of the non-catalytic Appel reaction and BET isotherms of SiO₂₍₇₀₀₎ and SiO_{2,700-Cl}. See DOI: 10.1039/x0xx00000x

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silica pretreated at 700, 500 and 200 °C under dynamic vacuum (10^{-5} torr)).



Scheme 1. A general reaction scheme for the synthesis of well-defined chlorinated silica by treatment with $(\text{COCl})_2/\text{POPh}_3$ in CHCl_3 .

As a chlorination strategy, we employ an atom-economic method utilizing stoichiometric amounts of $(\text{COCl})_2$ as the chlorinating agent and POPh_3 in catalytic amounts (Scheme 1). Interestingly, this method, generally applied as the catalytic Appel reaction in homogeneous organic synthesis,³² has never been used for the chlorination of oxide surfaces.

Experimental Section

General procedures

All air and moisture sensitive samples were handled in a glovebox and with standard Schlenk techniques under argon atmospheres. Chemicals were purchased from commercial sources and used as received. Solvents were dried, distilled, and degassed through freeze-pump-thaw cycles before use. $\text{SiO}_{2(700)}$, $\text{SiO}_{2(500)}$ and $\text{SiO}_{2(200)}$ (the subscripts 700, 500 and 200 refer to the treatment temperature in degrees °C) were prepared from Degussa Aerosil silica (specific surface area: $200 \text{ m}^2 \text{ g}^{-1}$) by partial dehydroxylation at 700, 500 and 200 °C, respectively under high vacuum (10^{-5} Torr) for 15 h. Elemental analyses were performed by the Mikroanalytisches Labor Pascher (Germany).

Instrumentation

IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer equipped with a controlled-atmosphere cell. Typically, 32 scans were accumulated for each spectrum (resolution 4 cm^{-1}). All liquid-state NMR spectra were recorded on Bruker Avance 400 MHz spectrometers using CD_2Cl_2 as the solvent. The chemical shifts were measured relative to the internal standard tetramethylsilane (TMS; ^1H or ^{13}C resonances appear at 0.00 ppm) present in CD_2Cl_2 . ^{31}P chemical shift was measured relative to 85% phosphoric acid ($\delta = 0$ ppm).

^{29}Si solid-state NMR spectra were recorded with a 400 MHz Bruker AVANCE III spectrometer. Experiments using the 400 MHz spectrometer employed a conventional double-resonance 4 mm CP/MAS probe. In each case the sample was packed into a zirconia rotor under an inert atmosphere inside a glovebox. Dry nitrogen gas was utilized for sample spinning to prevent degradation of the samples. For CP/MAS NMR experiments, the following sequence was used: 90° pulse on the proton channel (pulse length of $2.4 \mu\text{s}$), then a cross-polarization step with a contact time of typically 2 ms, and finally acquisition of the ^{29}Si NMR signals under the influence of high-power proton decoupling. The delay between the

scans was set to 5 s to allow for the complete relaxation of the ^1H nuclear magnetization, and the number of scans ranged between 30 000 and 50 000. An exponential apodization function corresponding to a line broadening between 80 and 150 Hz was applied prior to Fourier transformation. ^{29}Si chemical shifts are reported with respect to TMS.

Nitrogen adsorption/desorption isotherms were acquired on a Micromeritics ASAP 2420 instrument at 77 K. The analyses were carried out after degassing the samples at 150 °C under vacuum for 2 h. The surface areas of the samples were analysed by multipoint BET analysis method.

Preparation of materials 1-3

Synthesis of 1. A solution of oxalyl chloride (27 μL ; 0.309 mmol in 1 mL CHCl_3) was added to a slurry of $\text{SiO}_{2(700)}$ (1 g; ~ 0.3 mmol Si-OH) in 3 mL CHCl_3 under stirring. A solution of POPh_3 (12.52 mg; 0.045 mmol) in CHCl_3 (1 mL) was reacted with oxalyl chloride (4 μL ; 0.051 mmol) in a separate vessel. The latter mixture was added slowly to the $\text{SiO}_{2(700)}$ slurry over a period of 2 h at room temperature. The resulting mixture was stirred at r. t. for 2 h. Subsequently the organic phase was removed by filtration and the solid was washed with CHCl_3 (3×4 mL) followed by drying under dynamic vacuum for 12 h. The solid obtained was further degassed at 250 °C (under dynamic vacuum; $<10^{-5}$ mbar) for further 4 h to yield material **1**.

Synthesis of 1a. SOCl_2 (1g, 8.40 mmol, 28 equiv. with respect to the number of silanols) was added dropwise under stirring to a slurry of $\text{SiO}_{2(700)}$ (1g; ~ 0.3 mmol Si-OH) in CH_2Cl_2 (ca. 3 mL) at room temperature. After 2h, the organic phase was removed by filtration and the solid was washed with CH_2Cl_2 (3×4 mL). The material was dried under vacuum at room temperature (12 h) and degassed under dynamic vacuum ($<10^{-5}$ mbar) at 250 °C for further 4 h to yield material **1a**.

Synthesis of 1b. A solution of CCl_4 (28 μL ; 0.297mmol) and PPh_3 (78 mg, 0.297mmol) in 1 mL CH_2Cl_2 was added at r. t. to a slurry of $\text{SiO}_{2(700)}$ (575 mg, 0.1725 mmol Si-OH) in CH_2Cl_2 (ca. 3 mL) and stirred for 12 h. After filtration of the organic phase the solid was washed with CH_2Cl_2 (3×4 mL) and dried at 100 °C for 12h to afford material **1b**.

Synthesis of 2, 3. Materials **2** and **3** were prepared following the procedure described above for **1**. The following quantities of silica supports and reagents were used:

For **2**, a solution of oxalyl chloride (27 μL ; 0.309 mmol in 1 mL CHCl_3) was added to a slurry of $\text{SiO}_{2(500)}$ (714 mg; ~ 0.3 mmol Si-OH) in CHCl_3 (ca. 3 mL). A solution of POPh_3 (12.52 mg; 0.045 mmol) in CHCl_3 (1 mL) was separately reacted with oxalyl chloride (4 μL ; 0.051 mmol).

For **3**, a solution of oxalyl chloride (27 μL ; 0.309 mmol in 1 mL CHCl_3) was added to a slurry of $\text{SiO}_{2(200)}$ (385mg; ~ 0.3 mmol Si-OH) in CHCl_3 (ca. 3 mL). A solution of POPh_3 (12.52 mg; 0.045

mmol) in CHCl_3 (1 mL) was separately reacted with oxalyl chloride (4 μL ; 0.051 mmol).

Results and Discussion

The reaction between $\text{SiO}_2(700)$ (bearing well defined surface silanol groups; $\sim 0.23\text{--}0.3$ mmol Si-OH/g)¹⁸ and a stoichiometric mixture of $(\text{COCl})_2$ and POPh_3 in chloroform (Scheme 1) at room temperature followed by vacuum treatment at 250 °C yielded modified silica material **1**. FT-IR investigation of the latter material (Figure 1c) highlights a nearly complete disappearance of the characteristic $\equiv\text{Si-O-H}$ stretching vibration band ($\nu_{(\text{Si-O-H})}$) at 3747 cm^{-1} of $\text{SiO}_2(700)$ (Figure 1a) thus proving the occurrence of a quantitative reaction of the surface silanols.

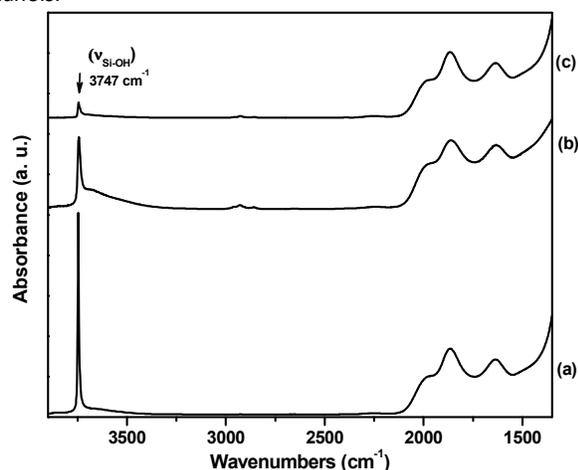


Figure 1. IR spectra of $\text{SiO}_2(700)$ (a); chlorinated silica prepared by treating $\text{SiO}_2(700)$ with SOCl_2 (b) and chlorinated silica prepared by treating $\text{SiO}_2(700)$ with $(\text{COCl})_2/\text{POPh}_3$ in CHCl_3 (c).

The quantitative replacement of the silanol groups by chlorine is evidenced by the elemental analysis data (Table 1) with the amount of newly introduced chlorine atoms matching the initial number of surface silanol moieties (See Table S1 for an overview of the amount of chlorine found by elemental analysis for each material). The absence of any accountable carbon and phosphorous residue (at least below detection limit) in **1** suggests that a clean, chlorinated surface could be achieved. Based on elemental analysis data, the use of a very large excess of nearly 30 equiv. SOCl_2 as the chlorinating agent to afford material **1a** following the procedure reported elsewhere,²⁴ led only to a moderate degree of chlorination of the silica surface (60%; 0.18 mmol Cl/g SiO_2 , Table 1). The microanalysis data of **1a** are in a good agreement with its infrared spectrum (Figure 1b) exhibiting only a moderate depletion of the intensity of characteristic $\equiv\text{Si-O-H}$ stretching vibration band ($\nu_{(\text{Si-O-H})}$) at 3747 cm^{-1} (Figure 1b). Moreover, the appearance of a broad signal in the 3500–3700 cm^{-1} region, generally attributed to the formation of hydrogen-bonded

vicinal silanols,¹⁵ suggests that, besides replacement of the silanols, other processes such as the opening of some siloxane bridges might occur when using this reagent. This phenomenon was observed also when alumina is treated with CCl_4 or COCl_2 .³³ Moreover, the elemental analysis of **1a** (Table S1) shows the presence of small amounts sulphur on this material. Considering that even the presence of traces of sulphur might lead to catalyst poisoning,³⁴ the presence of this element is undesirable especially if chlorinated silica is to be used as a support in catalysis.

Table 1: Chemical analysis data

Compound	OH (mmol/g)	Cl (mmol/g) ^a	Conv. (%) ^b	Ref.
$\text{SiO}_2(700)$	~ 0.3			15
1 ($\text{SiO}_2(700)\text{-Cl}$)		0.287	97	This work
1a ($\text{SiO}_2(700)\text{-Cl}$) ^c		0.18	60	This work
1b ($\text{SiO}_2(700)\text{-Cl}$) ^d		0.19	63	This work
$\text{SiO}_2(500)$	~ 0.42			8
2 ($\text{SiO}_2(500)\text{-Cl}$)		0.363	86	This work
$\text{SiO}_2(200)$	~ 0.78			15
3 ($\text{SiO}_2(200)\text{-Cl}$)		0.15	19	This work

^a Determined by microelemental analysis. ^b Determined by the ratio between the initial amounts of $\equiv\text{Si-OH}$ groups and the amount of chlorine found in the sample. ^c Prepared by treating $\text{SiO}_2(700)$ with excess of SOCl_2 according to Reference²⁴. ^d Prepared using $\text{CCl}_4/\text{PPh}_3$.

When the chlorination of $\text{SiO}_2(700)$ was carried out according to the non-catalytic Appel reaction protocol using a slight excess (1.7 equiv. with respect to the amount of silanols) of PPh_3 and CCl_4 ,³⁵ the resulting material (**1b**) displayed a moderate degree of chlorination (Table 1). Moreover, the IR spectrum of **1b** (Figure S1) showed the presence of a large hydrocarbon residue by the appearance of a band centred at 3000 cm^{-1} . We further investigated the scope of the chlorination reaction utilizing silica material $\text{SiO}_2(500)$ and $\text{SiO}_2(200)$ (reported to possess ~ 0.5 and ~ 0.8 mmol OH/g, respectively) with a lower degree of dehydroxylation.^{8, 15} Interestingly, chloride estimation of material **2** (Table 1) prepared (employing $\text{SiO}_2(500)$) under identical reaction conditions as for **1** revealed a degree of conversion of the surface silanols as high as

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86%. This observation is in a good agreement with the strong decrease in the intensity of the $\nu_{(\text{Si-O-H})}$ signal of the isolated silanols in the FT-IR spectrum of **2** (Figure 2d). A lower degree of chlorination (~20% according to the elemental analysis data in Table 1) was achieved when applying the same chlorination procedure to $\text{SiO}_{2(200)}$ to afford material **3**. For the latter compound, only a moderate decrease of the intensity of the broad stretching band of the hydrogen-bonded silanols in the 3300-3700 cm^{-1} region, and possibly, of the isolated silanols at 3747 cm^{-1} , was observed in the FT-IR spectrum (Figure 2f).

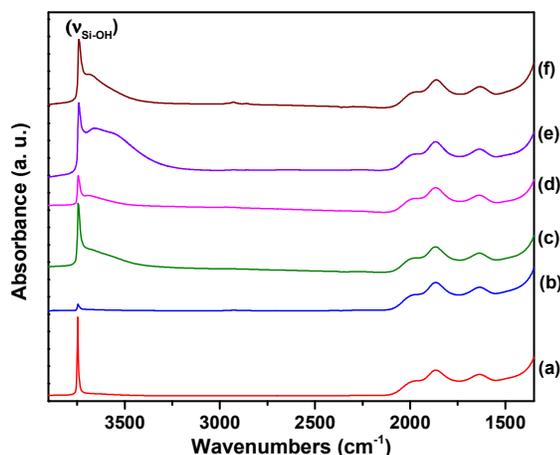


Figure 2. FT-IR spectra of $\text{SiO}_{2(700)}$ (a), **1** (b), $\text{SiO}_{2(500)}$ (c), **2** (d), $\text{SiO}_{2(200)}$ (e) and **3** (f).

Therefore, it is apparent that the efficiency of chlorination of the silica materials by the method in this study follows the order: $\text{SiO}_{2(700)} > \text{SiO}_{2(500)} > \text{SiO}_{2(200)}$. This observation is attributable to the intrinsically lower reactivity of the hydrogen-bridged silanols present on the surface of $\text{SiO}_{2(200)}$.³⁶

We performed a solid state ^{29}Si NMR study of chlorinated material **2** containing the highest molar loading of chlorine (0.36 mmol Cl/g of material). The spectrum obtained for the parent material $\text{SiO}_{2(500)}$ displays ^{29}Si resonances at -100.7 and -92.9 ppm which could be readily assigned, respectively, to the Q3 and Q2 Si-sites of the silica.³⁷ Interestingly, upon chlorination to afford **2**, an additional weak resonance centred at around -86 ppm was also observed. The latter peak might be due to the formation of $\equiv\text{Si-Cl}$ moieties being comparable to the shift assigned to such group in the literature for modified silsesquioxanes (-90.2 ppm).³⁸

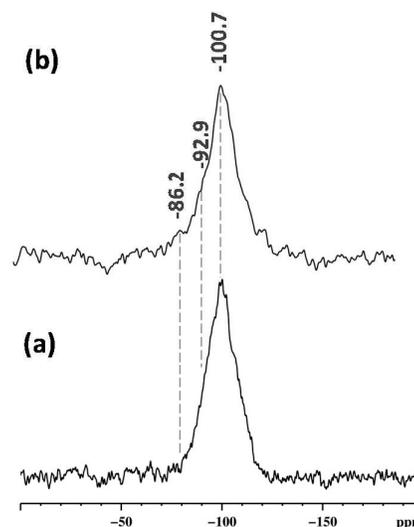
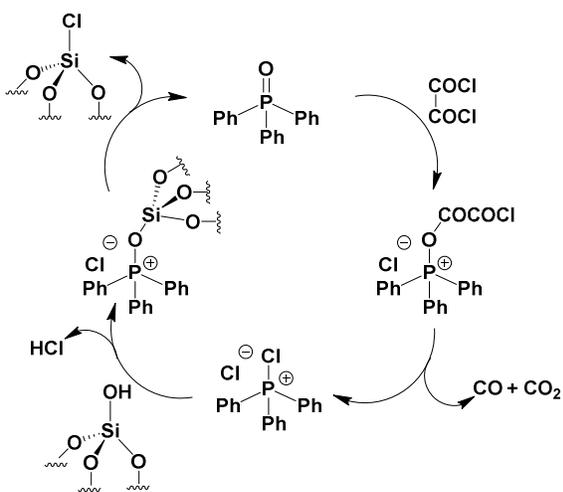


Figure 3. Solid-state ^{29}Si CP/MAS NMR of $\text{SiO}_{2(500)}$ (a) and $\text{SiO}_{2(500)-\text{Cl}}$ (b).

The BET surface areas of $\text{SiO}_{2(700)}$ and $\text{SiO}_{2(700)-\text{Cl}}$ from nitrogen sorption were determined. The isotherm plots are displayed in Figures S2, S3 of the ESI. The surface area of $\text{SiO}_{2(700)}$ (204 m^2/g) matches the specifications of the pristine commercial Aerosil-200 silica before dehydroxylation.³⁹ The surface area of chlorinated $\text{SiO}_{2(700)-\text{Cl}}$ (186 m^2/g) showed only a marginal decrease ($\approx 5\%$) with respect to the parent material. A similar phenomenon was observed in the past upon treatment and functionalization of $\text{SiO}_{2(700)}$ by the SOMC technique.¹⁸

To get further insight into the chlorination process we attempted to isolate and characterize the reaction intermediates and the products forming at various stages of the reaction. First, the addition of triphenyl phosphine oxide (^{31}P NMR signal at 29 ppm)³² to oxalyl chloride in dry CDCl_3 resulted in an instantaneous effervescence of colorless gaseous products. GC-MS analysis confirmed the presence of CO ($m/z = 28$) and CO_2 ($m/z = 44$) as the only products in the gas phase. After 2 minutes of reaction a white insoluble product was formed. Analysis by NMR spectroscopy confirmed this compound as a chlorotriphenylphosphonium chloride salt exhibiting a ^{31}P NMR signal at 64.6 ppm.³² In the following step, the silica substrate ($\text{SiO}_{2(700)}$) was added to the reaction mixture and stirring was continued for 2 h. After this contact time, the resulting solid material was filtered and washed three times with anhydrous CDCl_3 . Interestingly no traces of phosphorus containing organic species was found by NMR analysis of the filtrate solution. However, when the material was treated at 250 $^\circ\text{C}$ in vacuum (10^{-5} torr) for 4 h, a white solid product (presumably physisorbed on the silica surface) was found to separate out from the rest of the silica material by sublimation in a cold trap. Liquid state NMR analysis confirmed the identity of this material as the initial triphenylphosphine oxide catalyst showing a characteristic ^{31}P signal at 29 ppm and ^1H and ^{13}C signals corresponding to its aromatic groups. No trace of phosphorous was

detected in the solid-state NMR of the remaining silica material, consistent with the elemental analysis data of **1**.



Scheme 2. Proposed reaction mechanism towards the formation of $\equiv\text{Si-Cl}$ by reaction between $\equiv\text{Si-OH}$ and $\text{POPh}_3/(\text{COCl})_2$.

Taken together, these results are in agreement with the mechanism presented in Scheme 2 proceeding through the formation of a surface siloxyphosphonium salt and are consistent with the mechanism proposed for the chlorination of alcohols in the solution phase.³² The absence of carbon and phosphorus in the final material are the effect of the elimination of gaseous CO and CO₂ of oxalate and of the removal of the triphenylphosphine oxide catalyst upon thermal treatment at 250 °C under vacuum.

Conclusion

In summary, we have demonstrated the clean and quantitative chlorination of dehydroxylated silica surfaces by an amenable and straightforward catalytic method that allows the precise and careful replacement of the $\equiv\text{Si-OH}$ moieties with well-defined and isolated $\equiv\text{Si-Cl}$ functionalities without residues of carbon and phosphorus. This method, applied here for the first time to the functionalization of surfaces, can, in principle, be applied to the chlorination of several metal oxide supports displaying isolated -OH functionalities. The efficient replacement of the nucleophilic $\equiv\text{Si-OH}$ groups with $\equiv\text{Si-Cl}$ moieties might open new avenues of investigation for the grafting of nucleophilic inorganic, organometallic and organic fragments on well-defined silica surfaces leading to the development of unprecedented, surface-anchored isolated catalysts. Furthermore, the reported method could be applied for the clean functionalization of mesoporous fibrous nanosilicas such as KCC-1^{6, 40} that is emerging as an outstanding support in catalysis.^{19, 41, 42} The abovementioned potential developments are currently under investigation.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- S. Soled, *Science*, 2015, **350**, 1171-1172.
- P. Munnik, P. E. de Jongh and K. P. de Jong, *Chem. Rev.*, 2015, **115**, 6687-6718.
- J. Liang, Z. Liang, R. Zou and Y. Zhao, *Adv. Mater.*, 2017, **29**, 1701139.
- R. Luque, A. M. Balu, J. M. Campelo, M. D. Gracia, E. Losada, A. Pineda, A. A. Romero and J. C. Serrano-Ruiz, in *Catalysis*, ed. J. J. Spivey and M. Gupta, The Royal Society of Chemistry, Cambridge, 2012, vol. 24, pp. 253-280.
- S. E. Lehman and S. C. Larsen, *Environ. Sci.: Nano*, 2014, **1**, 200-213.
- A. Maity and V. Polshettiwar, *ChemSusChem*, 2017, **10**, 3866-3913.
- J. D. A. Pelletier and J.-M. Basset, *Acc. Chem. Res.*, 2016, **49**, 664-677.
- C. Copéret, M. Chabanas, R. Petroff Saint-Arroman and J.-M. Basset, *Angew. Chem., Int. Ed.*, 2003, **42**, 156-181.
- C. Copéret, A. Comas-Vives, M. P. Conley, D. P. Estes, A. Fedorov, V. Mougél, H. Nagae, F. Núñez-Zarur and P. A. Zhizhko, *Chem. Rev.*, 2016, **116**, 323-421.
- Z. S. Qureshi, A. Hamieh, S. Barman, N. Maity, M. K. Samantaray, S. Ould-Chikh, E. Abou-hamad, L. Falivene, V. D'Elia, A. Rothenberger, I. Llorens, J.-L. Hazemann and J.-M. Basset, *Inorg. Chem.*, 2017, **56**, 861-871.
- Y. Bouhoute, A. Garron, D. Grekov, N. Merle, K. C. Szeto, A. De Mallmann, I. Del Rosal, L. Maron, G. Girard, R. M. Gauvin, L. Delevoeye and M. Taoufik, *ACS Catal.*, 2014, **4**, 4232-4241.
- V. Mougél and C. Copéret, *ACS Catal.*, 2015, **5**, 6436-6439.
- N. Maity, S. Barman, E. Callens, M. K. Samantaray, E. Abou-Hamad, Y. Minenkov, V. D'Elia, A. S. Hoffman, C. M. Widdifield, L. Cavallo, B. C. Gates and J.-M. Basset, *Chem. Sci.*, 2016, **7**, 1558-1568.
- J.-M. Basset, C. Coperet, D. Soulivong, M. Taoufik and J. T. Cazat, *Acc. Chem. Res.*, 2010, **43**, 323-334.
- V. D'Elia, H. Dong, A. J. Rossini, C. M. Widdifield, S. V. C. Vummaleti, Y. Minenkov, A. Poater, E. Abou-Hamad, J. D. A. Pelletier, L. Cavallo, L. Emsley and J.-M. Basset, *J. Am. Chem. Soc.*, 2015, **137**, 7728-7739.
- M. J. Kelly, A. Barthel, C. Maheu, O. Sodpiban, F.-B. Dega, S. V. C. Vummaleti, E. Abou-Hamad, J. D. A. Pelletier, L. Cavallo, V. D'Elia and J.-M. Basset, *J. CO₂ Util.*, 2017, **20**, 243-252.
- Larmier, W.-C. Liao, S. Tada, E. Lam, R. Verel, A. Bansode, A. Urakawa, A. Comas-Vives and C. Copéret, *Angew. Chem., Int. Ed.*, 2017, **56**, 2318-2323.
- S. Barman, N. Maity, K. Bhatte, S. Ould-Chikh, O. Dachwald, C. Haeßner, Y. Saih, E. Abou-Hamad, I. Llorens, J.-L. Hazemann, K. Köhler, V. D'Elia and J.-M. Basset, *ACS Catal.*, 2016, **6**, 5908-5921.
- Z. S. Qureshi, P. B. Sarawade, I. Hussain, H. Zhu, H. Al-Johani, D. H. Anjum, M. N. Hedhili, N. Maity, V. D'Elia and J.-M. Basset, *ChemCatChem*, 2016, **8**, 1671-1678.
- A. Bendjeriou-Sedjerari, J. M. Azzi, E. Abou-Hamad, D. H. Anjum, F. A. Pasha, K.-W. Huang, L. Emsley and J.-M. Basset, *J. Am. Chem. Soc.*, 2013, **135**, 17943-17951.

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Journal Name

- 21 A. Bendjeriou-Sedjerari, J. Sofack-Kreutzer, Y. Minenkov, E. Abou-Hamad, B. Hamzaoui, B. Werghi, D. H. Anjum, L. Cavallo, K.-W. Huang and J.-M. Basset, *Angew. Chem., Int. Ed.*, 2016, **55**, 11162-11166.
- 22 D. Seebach, *Angew. Chem., Int. Ed. Eng.*, 1979, **18**, 239-258.
- 23 Y. Kamitori, M. Hojo, R. Masuda, T. Kimura and T. Yoshida, *J. Org. Chem.*, 1986, **51**, 1427-1431.
- 24 H. N. Karade, M. Sathe and M. P. Kaushik, *Molecules*, 2007, **12**, 1341-1351.
- 25 B. Datta and M. A. Pasha, *Bull. Korean Chem. Soc.*, 2012, **33**, 2129-2130.
- 26 H. Firouzabadi, N. Iranpoor, H. Hazarkhani and B. Karimi, *J. Org. Chem.*, 2002, **67**, 2572-2576.
- 27 B. Karami, V. Ghashghaee and S. Khodabakhshi, *Catal. Commun.*, 2012, **20**, 71-75.
- 28 S. Khodabakhshi and B. Karami, *Catal. Sci. Technol.*, 2012, **2**, 1940-1944.
- 29 B. Karami, M. Kiani, S. J. Hosseini and M. Bahrami, *New J. Chem.*, 2015, **39**, 8576-8581.
- 30 A. M. Jadhav, S. K. Krishnammagari, J. T. Kim and Y. T. Jeong, *Tetrahedron*, 2017, **73**, 5163-5169.
- 31 N. Ahmed and Z. N. Siddiqui, *J. Mol. Catal. A: Chem.*, 2014, **387**, 45-56.
- 32 R. M. Denton, J. An, B. Adeniran, A. J. Blake, W. Lewis and A. M. Poulton, *J. Org. Chem.*, 2011, **76**, 6749-6767.
- 33 J.-M. Basset, *Rev. Chim. Miner.*, 1968, **5**, 879-895.
- 34 D. C. Elliott and R. R. Maggi, 1997, Workshop Report: Catalytic Processes, In *Developments in Thermochemical Biomass Conversion*, ed. A. V. Bridgwater and D.G.B. Boocock, Springer, Dordrecht, 1997, pp. 1626-1630.
- 35 E. Årstad, A. G. M. Barrett, B. T. Hopkins and J. Köbberling, *Org. Lett.*, 2002, **4**, 1975-1977.
- 36 P. Van Der Voort, I. Gillis-D'Hamers, K. C. Vrancken and E. F. Vansant, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 3899-3905.
- 37 D. W. Sindorf and G. E. Maciel, *J. Am. Chem. Soc.*, 1983, **105**, 1487-1493.
- 38 R. Duchateau, H. C. L. Abbenhuis, R. A. van Santen, S. K. H. Thiele and M. F. H. van Tol, *Organometallics*, 1998, **17**, 5222-5224.
- 39 AEROSIL-200, <https://www.ulprospector.com/en/eu/PersonalCare/Detail/688/26722/AEROSIL-200> (accessed February 2018).
- 40 V. Polshettiwar, D. Cha, X. Zhang and J. M. Basset, *Angew. Chem., Int. Ed.*, 2010, **49**, 9652-9656.
- 41 M. Dhiman, B. Chalke and V. Polshettiwar, *J. Mater. Chem. A*, 2017, **5**, 1935-1940.
- 42 R. Singh, R. Bapat, L. Qin, H. Feng and V. Polshettiwar, *ACS Catal.*, 2016, **6**, 2770-2784.

Graphical Abstract

Clean Chlorination of Silica Surfaces by a Single-site Substitution Approach

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Unveiling a clean, selective chlorination method for the quantitative substitution of well-defined non-hydrogen bonded silanol groups of the silica surface.

