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Sol–Gel Synthesis of Porous Organosilicate Phosphorylated Ion Exchangers: Precursor Chemistry, Pore Control and Relevance to Uzbekistan's Mining Sector

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Abstract. Phosphorylated hybrid ion exchangers prepared by the sol–gel route combine the chemical robustness of a silicate framework with the strong cation affinity of acidic phosphorus groups. This article reviews how precursor choice, catalysis, templating and drying determine the architecture of porous organosilicate phosphorylated materials. Particular attention is given to the hydrolytic fragility of Si–O–P linkages, which has pushed the field towards non-hydrolytic condensation, towards metal phosphonate networks, and towards organosilanes in which phosphorus is anchored through a stable carbon bridge. Soft-template formation of ordered mesopores is discussed as the main tool for making phosphate sites accessible, and recent applications, from lead and cadmium removal to lithium recovery with ionogels, are summarised. The final section places the subject in the context of Uzbekistan, where reported uranium output rose from about 3.1 thousand tonnes of uranium in 2014 to 3.5 thousand tonnes in 2019, and where sulfuric-acid-based processing makes acid-stable, selective sorbents a topic of practical interest.

Keywords: Sol–gel process; organosilicate; phosphorylation; ion exchange; mesoporous materials; Si–O–P bond; templating; uranium; Uzbekistan

Ion exchange is among the oldest separation principles in chemistry, yet the materials that carry it out keep changing. Crystalline zirconium phosphate, prepared in well-defined form by Clearfield and Stynes in 1964, showed that acidic phosphate groups held in a rigid inorganic lattice can bind cations strongly even in acidic and aggressive media, and it opened a long line of research on acid salts of tetravalent metals. Such crystalline phosphates, however, are usually obtained as fine powders with limited and poorly adjustable porosity, which restricts how fast ions can reach the exchange sites.

Sol–gel chemistry offers a different starting point. Because the network is built from molecular precursors in solution at or near room temperature, organic groups that would not survive a ceramic firing can be built directly into the solid. The same flexibility explains why ordered mesoporous silicas became so influential after the M41S family was reported in 1992 and the larger-pore SBA-15 silica in 1998, and why periodic mesoporous organosilicas, in which organic bridges sit inside the pore walls, followed in 1999. Placing phosphorus-based acidic groups on such frameworks combines the accessible pore system of a mesoporous silicate with the cation-binding capacity of a phosphate or phosphonate.

The aim of this article is to organise recent work on this class of materials around three questions: how phosphorus can be incorporated without sacrificing the stability of the network, how the pore structure can be tuned so that the phosphorus sites are actually reachable, and where such sorbents may become useful. The last question is examined with national data from Uzbekistan, a country in which mining and hydrometallurgy are major industries.

In the classical silica system, tetraethyl orthosilicate (TEOS) reacts with water in an alcohol solvent in the presence of an acid or base catalyst. Alkoxide groups are first replaced by hydroxyl groups, and the silanols then condense with each other or with remaining alkoxide groups to form siloxane bridges:

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≡Si–OR + H_2O → ≡Si–OH + ROH (1)
≡Si–OH + HO–Si≡ → ≡Si–O–Si≡ + H_2O (2)
≡Si–OR + HO–Si≡ → ≡Si–O–Si≡ + ROH (3)

Which of these steps dominates depends mainly on pH. Under acidic conditions hydrolysis is fast and condensation is slow, which favours weakly branched, polymer-like species; under basic conditions condensation catches up and compact, particulate sols are formed. A study of silica xerogels showed in practical terms how pH, the nature of the acid catalyst and the aging time each leave a measurable imprint on pore characteristics after drying. Titanium and zirconium alkoxides are considerably more reactive towards water than TEOS, so they are normally handled with chelating additives or in non-aqueous media. That reactivity is useful for phosphates: lithium-conducting titanium phosphates, for example, have been obtained by a sol–gel process in which the titanium precursor and the phosphorus source are brought together in solution.

Four strategies are used in the literature. In the first, an inorganic phosphorus source such as phosphoric acid is co-condensed with the alkoxide so that phosphorus becomes part of the oxide network, giving silicophosphates or, with metal alkoxides, zirconium, titanium or tin phosphates. In the second, phosphate or phosphonate esters serve as the phosphorus source. In the third, an organosilane that already carries a phosphorus-containing arm, for instance diethylphosphatoethyltriethoxysilane, is co-condensed with TEOS; the organic tether then keeps phosphorus covalently attached to the silica backbone, and the ester groups are removed afterwards to expose the acidic P–OH sites. In the fourth, phosphorus is grafted onto a silica network that has been prepared beforehand. Reviews of sol–gel routes to phosphorus- and zirconium-containing hybrids describe this family of methods as a green approach, in part because it works under mild conditions. The overall sequence is shown in Figure 1, and the characteristic features of each route are compared in Table 1.

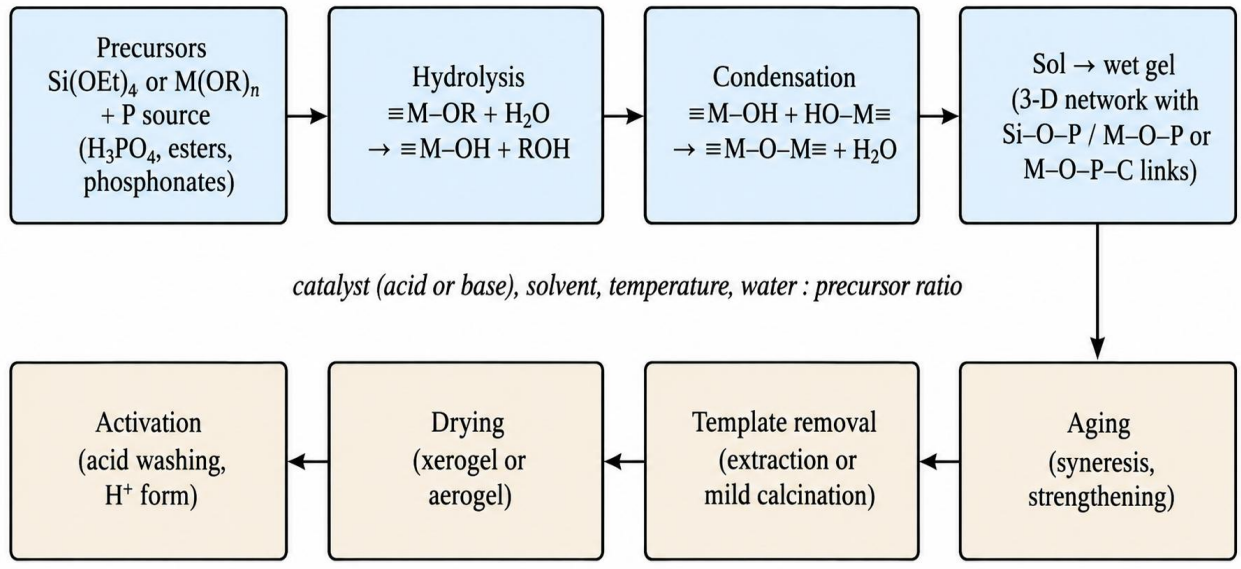


Figure 1. General sequence of sol–gel preparation of a phosphorylated hybrid ion exchanger, from molecular precursors to the activated H^+ form (M = Si, Ti, Zr, Sn;
R = alkyl).

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Table 1. Comparison of sol–gel routes used to incorporate phosphorus into silicate and metal oxide networks.

Route	Phosphorus linkage to the network	Main advantage	Main limitation
Hydrolytic co-condensation with H_3PO_4 or phosphate esters	Si–O–P (or M–O–P) bridges	Simple, inexpensive, one-pot	Si–O–P bonds hydrolyse; phase separation and phosphorus loss are possible
Non-hydrolytic condensation (halide–ether or ester routes)	M–O–P / M–O–P–C in the network	Mesoporous phosphonates with narrow pore-size distribution	Moisture-free handling; narrower precursor scope
Co-condensation of a phosphorus-bearing organosilane with TEOS	Si–C bond to the tether; P attached through carbon (and oxygen)	Covalent, uniform distribution of sites	Ester deprotection step required; precursors are costly
Post-synthetic grafting on pre-formed silica	Surface Si–O–P or Si–C–P	Pore structure fixed before functionalisation	Possible pore blocking; uneven coverage
Metal phosphate or phosphonate hybrids and polymer composites (Zr, Ti, Sn)	M–O–P, often with conducting polymer	Strong cation affinity; improved mechanical strength	Lower silica content; selectivity depends on the metal

Table compiled by the author from the literature discussed in the text; entries are qualitative.

The central difficulty of the hydrolytic route is that the Si–O–P linkage is not stable in the presence of water. A careful examination of solids containing Si–O–P bonds asked directly whether the hydrolytic sol–gel route is a suitable synthesis strategy, and the answer was a cautious one: under hydrolytic conditions the bonds can break, which leads to phase separation or an incompletely formed network, so that part of the phosphorus is present as free phosphate rather than as a built-in site. For an ion exchanger this matters twice over. Capacity is lost, and phosphorus can leach into the treated solution, which defeats the purpose of purification.

Three responses can be distinguished. The first is to avoid water during condensation altogether. Non-hydrolytic sol–gel routes have been used to prepare zirconium phosphonates with controlled mesoporosity, high surface areas and uniform pore sizes. The second is to move phosphorus out of the hydrolytically vulnerable position by using phosphonates or organosilanes, where phosphorus is tied to carbon and the siloxane network is formed by ordinary Si–O–Si bonds. The third is to rely on metal–oxygen–phosphorus bonds, which are generally more resistant than Si–O–P, and to combine them with an organic component. Composite cation exchangers in which a conducting polymer is integrated with a zirconium phosphate matrix by sol–gel processing have been reported to show improved mechanical strength and exchange

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kinetics, and a poly(o-anisidine)–tin(IV) silicophosphate nanocomposite has been used for the selective removal of cadmium(II).

A practical consequence follows from these findings. A sorbent should not be judged by its initial capacity alone. Phosphorus leaching in the working medium and capacity retained after repeated acid regeneration cycles are equally decisive, and they are the tests on which the hydrolytic Si–O–P materials are most likely to fail.

Porosity decides whether the phosphorus sites can be reached by hydrated ions. Soft templates, that is surfactants or block copolymers that assemble into micelles, are the usual tool: the silicate and phosphorus precursors condense around the micelles, and removal of the template leaves an ordered system of mesopores whose walls carry the functional groups (Figure 2). Dual-template strategies have been used to prepare hollow periodic mesoporous organosilica nanoparticles whose size, cavity and shell thickness can be set independently, and hollow mesoporous organosilica nanospheres of different sizes have been described as well. When this idea is transferred to phosphorylated systems, the aim is that phosphorus ends up on the pore surface and not buried in the wall.

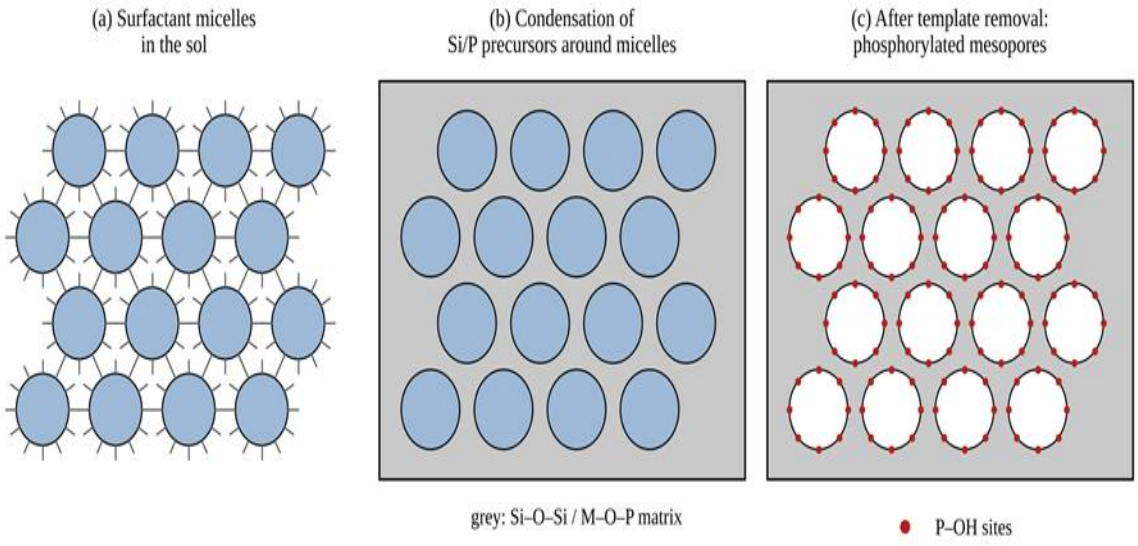


Figure 2. Schematic of soft-template formation of a phosphorylated mesoporous organosilicate: (a) surfactant micelles in the sol, (b) condensation of the silicon and phosphorus precursors around the micelles, (c) accessible pore system lined with P–OH groups after template removal. The drawing is illustrative and not to scale.

Template removal deserves attention in its own right. High-temperature calcination, which is routine for pure silica, oxidises organic groups and is therefore unsuitable for hybrid materials; solvent extraction under mild acidic conditions is the more appropriate choice. Drying is another critical step, because capillary forces in the evaporating pore liquid can collapse the network, which is why supercritical drying (aerogels) retains more porosity than ordinary evaporation (xerogels). The synthetic variables and their usual influence are summarised in Table 2.

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Table 2. Principal synthesis variables and their general influence on the texture and ion-exchange behaviour of phosphorylated sol–gel materials.

Variable	General effect on texture	Consequence for ion exchange
Catalyst and pH	Acidic: weakly branched polymers; basic: compact particles	Determines pore size and the rate at which sites become accessible
Aging time	Strengthens the gel network and shifts pore characteristics	Mechanical stability during repeated regeneration
Water : precursor ratio	Controls extent of hydrolysis before condensation	Affects completeness of network and retention of phosphorus
Template type and removal	Sets pore size and order; extraction preserves organic groups	Accessibility of P–OH sites
Drying route	Xerogel: shrinkage; aerogel: higher retained porosity	Kinetics and capacity per gram
Phosphorus loading	Excess can disturb network formation or block pores	Capacity rises only up to the point where sites remain accessible

Qualitative summary based on general sol–gel principles and the studies cited in the text.

The strong affinity of phosphate groups for heavy-metal cations explains the interest in environmental applications. Silicophosphate nanocomposites have shown pronounced selectivity for cadmium, and sol–gel routes have also been applied to non-silicate sorbents, such as porous amorphous magnesium hydroxide for lead(II) adsorption, which provides a useful reference point for what a purely inorganic sol–gel sorbent can achieve.

Beyond heavy metals, the same chemistry reaches other fields. Phosphoroxy-functionalised ionogels, in which an ionic liquid is confined in a sol–gel-derived matrix, have been used for the selective extraction of lithium ions from the mother liquor remaining after Li_2CO_3 precipitation; the wider ionogel literature explains how sol–gel chemistry is adapted to build solid electrolytes. Silica gels decorated with zwitterionic phosphorylcholine groups in a one-pot sol–gel synthesis combine a high degree of hydration with antifouling character, which is relevant for biomedical uses. Zirconium phosphates and phosphonates are also well established as catalysts, and tuning the hydrophobicity of related aluminosilicates with trimethylsilyl groups has been shown to raise catalytic activity. Both observations remind us that acidity and hydrophobicity can be adjusted through the choice of the organic substituent. Finally, work on silica–epoxy nanocomposites shows that organosilane coupling in sol–gel systems is a reliable way to bond the inorganic and organic phases covalently, which is the same principle that keeps phosphorus-bearing groups attached to the support.

Uzbekistan offers a concrete setting in which selective sorbents are of interest. According to figures released by the Navoi Mining and Metallurgical Combinat and reported in 2020, uranium output grew steadily from 3,128 t U in 2014 to 3,445 t U in 2018, and the World Nuclear Association gave 3,500 t U for both 2019 and 2020, which placed the country fifth in the world and corresponded to about 6.4 per cent of global production. In the same release the country’s

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uranium reserves were put at about 139 thousand tonnes, tenth in the world. The combinat is the only natural-uranium producer in the country, and the product is exported in full. The UN Energy Statistics Yearbook lists a different figure for 2016–2018 (2,404 t), so different sources do not fully agree on the earlier part of the series. For 2024 the World Nuclear Association estimate is 4,000 t, and the presidential press service later reported 7,000 t mined in 2025, which would be an increase of 75 per cent over the 2024 estimate (Figure 3 and Table 3). For comparison, Kazakhstan was reported at 25.8 thousand tonnes in the same statement.

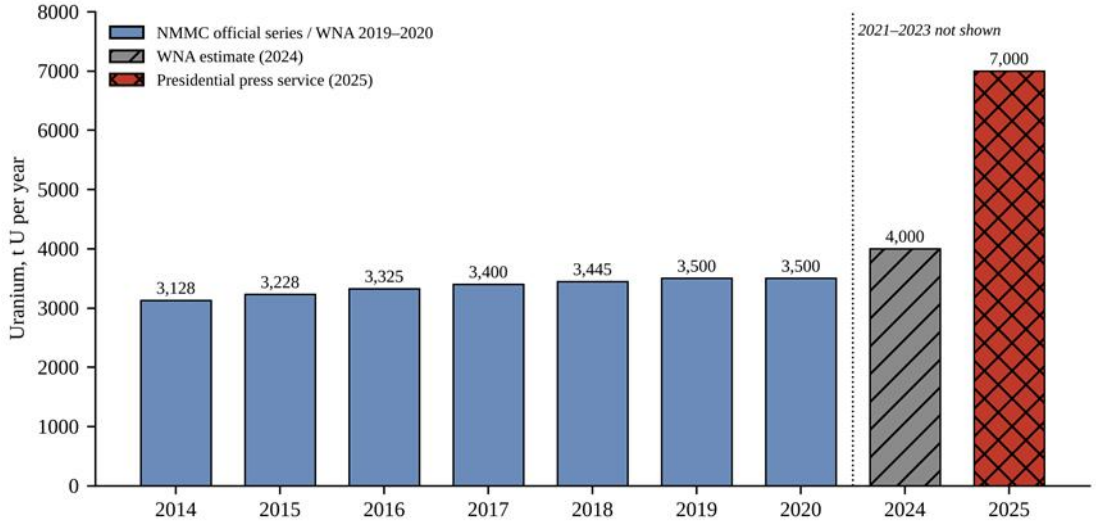


Figure 3. Reported uranium production of Uzbekistan in selected years. Data for 2021–2023 are not included because they were not retrieved for this review. The 2016–2018 values of the official series differ from those in the UN Energy Statistics Yearbook (2,404 t U per year).

Table 3. Selected indicators of Uzbekistan's uranium sector according to publicly reported data.

Indicator	**Value**	**Reporting body (year of statement)**
Uranium production, 2019 and 2020	3,500 t U per year	World Nuclear Association (2021)
Position among world producers, 2020	5th	World Nuclear Association (2021)
Share of world production	about 6.4 %	Navoi Mining and Metallurgical Combinat (2020)
World production, 2020	47,731 t U	World Nuclear Association (2021)
Identified reserves	about 139 thousand t U (10th)	National statement (2020); presidential press service (2025)
Estimated production, 2024	4,000 t U	World Nuclear Association
Reported mining output, 2025	7,000 t U	Presidential press service

Values are reproduced as published; they have not been independently verified.

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Two facts from official statements make the topic relevant to this article. First, the country's uranium is produced in processes that depend on sulfuric acid; in 2025 the authorities ordered the faster commissioning of sulfuric acid capacity in the Navoi region precisely to secure stable output and called for more processing capacity. Second, uranium recovery from acidic leach liquors is a standard use of ion exchange. In such a setting a sorbent must function at low pH, which in turn argues for the approaches discussed in Section 3: phosphonate-type linkages and metal–oxygen–phosphorus networks rather than hydrolytically labile Si–O–P bonds. We stress that this is a prospect and not a demonstrated result. The sources reviewed here do not report pilot trials of sol–gel phosphorylated organosilicates in Uzbek hydrometallurgical plants, and testing in real leach solutions would be the obvious next step.

Sol–gel synthesis provides a controllable route to hybrid ion exchangers in which acidic phosphorus groups are distributed through a porous silicate framework. The main obstacle is the hydrolytic instability of Si–O–P bonds; it has been addressed by non-hydrolytic condensation, by carbon-bridged phosphorus anchoring and by metal phosphate networks. Soft templating and careful drying give access to mesoporous architectures that make the sites reachable, and the resulting materials have been applied to heavy metals, lithium recovery, biomedical surfaces and catalysis. For Uzbekistan, where uranium output is reported to have grown substantially in recent years and acid-based processing is central, acid-stable phosphorylated sorbents deserve experimental evaluation. A convincing study should report capacity, selectivity in the presence of competing ions, phosphorus leaching and performance over repeated regeneration cycles.

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