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Catalytic behavior of hexaphenyldisiloxane in the synthesis of pyrite FeS₂

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Functional small molecules afford opportunities to direct solid-state inorganic reactions at low temperatures. Here, we use catalytic amounts of organosilicon molecules to influence the metathesis reaction: $\text{FeCl}_2 + \text{Na}_2\text{S}_2 \rightarrow 2\text{NaCl} + \text{FeS}_2$. Specifically, hexaphenyldisiloxane ($(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$) is shown to increase pyrite yields in metathesis reactions performed at 150 °C. *In situ* synchrotron X-ray diffraction (SXRD) paired with differential scanning calorimetry (DSC) reveals that diffusion-limited intermediates are circumvented in the presence of $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$. Control reactions suggest that the observed change in the reaction pathway is imparted by the Si–O functional group. ¹H NMR supports catalytic behavior, as $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ is unchanged *ex post facto*. Taken together, we hypothesize that the polar Si–O functional group coordinates to iron chloride species when NaCl and Na₂S₄ form, forming an unidentified, transient intermediate. Further exploration of targeted small molecules in these metathesis reaction provides new strategies in controlling inorganic materials at low-temperatures.

The use of small functional molecules to direct the outcome of a chemical reaction is foundational to solution-based synthetic chemistry, where catalysts and additives change activation barriers along the reaction pathway. Due to the high thermal energy barriers to diffusion, the reaction conditions of solid-state materials synthesis exceed the temperatures where most molecules are stable, or can impart selectivity, thus limiting the degree of kinetic control attainable in these reactions.¹ There are examples of inorganic materials syntheses that take advantage of small molecules in solution, such as incorporation of weak Lewis acid or base additives to assist atom transfer in synthesizing transition metal phosphides and chalcogenides.² These solution-based

syntheses can be expanded through step-wise cation or anion exchange reactions that use molecules like $(\text{CH}_3)_3\text{Si}-(\text{S}/\text{Se})$ and TOP to coordinate and transfer atoms into specific lattice sites.^{3,4} For solid-state synthesis, reactions must proceed at temperatures where these molecules do not decompose in order to take advantage of their targeted functional groups.

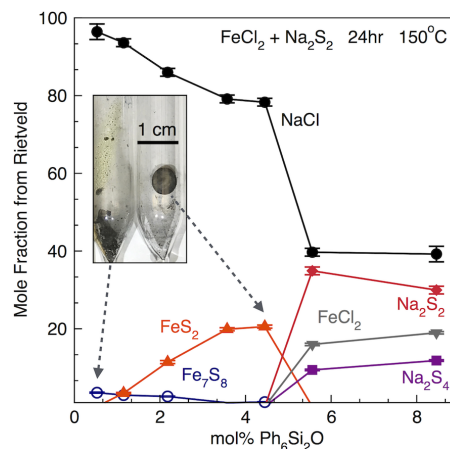


Fig. 1 Mole fraction of crystalline products from Rietveld refinements of PXRD data when varying the mol% concentration of $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ in metathesis reactions at 150 °C for 24 h. The inset shows an intact reaction pellet when using 4.5 mol% $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ as compared to the reaction with 0.5 mol% $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$. At 0.5 mol% $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$, the pellet disintegrated from a rapid propagation event leaving condensed sulfur.

Exchange reactions, including metathesis, provide low-temperature solid-state syntheses where reaction kinetics can be controlled using small molecules to direct product selectivity. For example, the addition of molecules like H₂O and $(\text{C}_6\text{H}_5)_3\text{P}$ has been shown to aid in atom transfer and intermediate conversion in solid-state metathesis reactions, which permits the stabilization of metastable phases like superconducting CuSe₂ with no applied pressure.^{5,6} Exploring more functional molecules and understanding their role in changing reaction kinetics will permit more predictive synthesis of inorganic materials.

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† Electronic Supplementary Information (ESI) available:

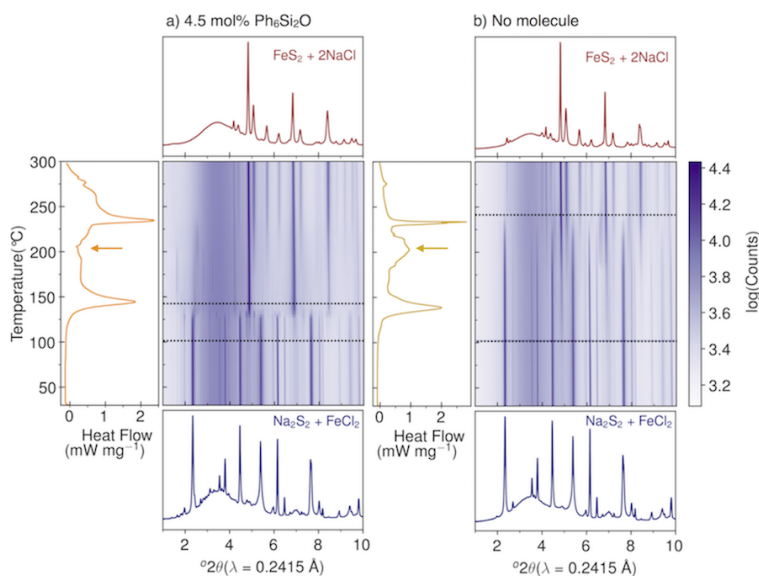


Fig. 2 *In situ* SXR D results of the reaction $\text{Na}_2\text{S}_2 + \text{FeCl}_2$ using a) 4.5 mol% $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ and b) with no molecular additive heating at 10 °C/min to 300 °C. DSC plots are appended to a) and b) to compare crystallization exotherms. Dotted lines denote the start and stop of reactive zones in the diffraction data. The reaction proceeds from precursors, reactive intermediates, and finally products. The colored arrows denote the exotherm, or lack there of, for crystalline intermediates.

In this work, we study a metathesis reaction $(\text{Na}_2\text{S}_2 + \text{FeCl}_2 \longrightarrow \text{FeS}_2 + 2\text{NaCl})$ that produces pyrite FeS_2 and attempt to influence the reaction pathway at low temperatures. The neat reaction, proceeds to completion at 350 °C for 24 h, whereas temperatures lower than 350 °C result in diffusion-limited products (Na_2S_4 , Na_2S_5 , NaFeS_2 , and Fe_{1-x}S), as we have previously showed.⁷ In contrast, temporary exposure to $\text{H}_2\text{O}(\text{g})$ allows the reaction to proceed to completion at temperatures as low as 150 °C, but it is not known how this is accomplished or if any selectivity is imparted.

Here, organosilicon molecules are considered for their physical properties and role as a mediator for ion transport (e.g., halogen transfer⁸, ferrosiloxane adducts⁹, Table S1) when changing the Si–X (Si–O–Si, Si–OH, Si–Cl) functional group. We demonstrate that the addition of $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ and $(\text{C}_6\text{H}_5)_3\text{SiOH}$ to inorganic precursors selectively yields crystalline NaCl and FeS_2 at low concentrations and reaction times. Hexaphenyldisiloxane, a weak Lewis base, appears to catalytically lower the energy barrier to formation of FeS_2 . Varying the concentration of $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ changes the reaction kinetics, in which a narrow concentration range (2-5 mol%) of the molecule produces the most pyrite. ¹H NMR reveals that the molecule remains unchanged *ex post facto*. Analysis of the reaction pathways using *in situ* synchrotron X-ray diffraction (SXR D) and differential scanning calorimetry reveals that $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ changes the reaction pathway by reducing the observed number of diffusion limited intermediates. Changing the concentration of the molecule tunes the reaction kinetics from vigorous propagation events to a more mild pathway that increases the yield of FeS_2 . Pairing solid-state precursors with functional small molecules provides new avenues for synthesizing functional inorganic materials at low temperatures.

The presence of $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ yields FeS_2 in metathesis reactions performed at temperatures that are significantly lower than

for the neat reaction. PXRD data in Figure S1 of the neat metathesis reaction show formation of crystalline NaCl , small amounts of pyrite FeS_2 , along with high amounts of unreacted Na_2S_2 precursor (Table S2). As compared to the metathesis reaction without a molecular additive, the PXRD results using 4.5 mol% $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ (MP: 225 °C) show an increase in the crystallinity and phase fraction of FeS_2 and NaCl (~4:1 $\text{NaCl}:\text{FeS}_2$ in Fig. S1). After 24 h at 150 °C, the reaction has not proceeded to completion (i.e., 2:1 $\text{NaCl}:\text{FeS}_2$ in Figure 1), yet longer reaction times (> 24 h) yield more FeS_2 , suggesting that growth of FeS_2 is still limiting the reaction at 150 °C. Nonetheless, as the $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ concentration increases from 0.5 mol% to 4.5 mol%, the mol% phase fraction of the FeS_2 in the PXRD results increases (Table S2; Fig. 1). At higher mol% concentrations ($x \geq 4.5$ mol%), the products are comprised of Na_2S_2 and Na_2S_4 . At 0.5 mol% $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$, the reaction self-propagates rapidly, as indicated by complete pellet deformation and the presence of sulfur condensed on the ampule (Fig 1). PXRD reveals NaCl and Fe_7S_8 but no FeS_2 supporting previous studies of highly exergonic metathesis reactions, such as $\text{MoCl}_5 + \frac{5}{2}\text{Na}_2\text{S}$, where similar disproportionation of alkali sulfides results in decomposition of sulfide anions to sulfur.^{10,11} Taken together, these observations indicate that $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ directly influences the pathway and the reaction rate.

The decrease in reactivity at higher molecular loadings ($x \geq 4.5$ mol%) is explained by the relative volume fractions, which results in a decrease in physical contact between precursors. For perspective, 8.5 mol% $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ represents ~80% by volume of the total precursor mixture. In previous metathetical preparations of transition-metal borides and nitrides where the reaction is highly exothermic, additional alkali-metal halide salts are added to precursors to act as a heat sink.¹¹ Hexaphenyldisiloxane also appears to function similarly. At molecular loadings where

the reaction proceeds to iron sulfide products ($0.5 < x \leq 4.5$ mol%), the $(C_6H_5)_6Si_2O$ molecule is hypothesized to provide a heat sink to dampen the observed propagation kinetics observed at 0.5 mol% (Fig. 1). Thus, reactions with 4.5 mol% $(C_6H_5)_6Si_2O$ do not propagate, which results in higher yields of FeS_2 .

Temperature-dependent *in situ* synchrotron X-ray diffraction experiments reveal that $(C_6H_5)_6Si_2O$ reduces the number of crystalline intermediates observed along the reaction pathway. Figure 2 presents combined *in situ* SXRD and differential scanning calorimetry (DSC) experiments heated at 10 °C/min to 300 °C. Metathesis reactions with 4.5 mol% $(C_6H_5)_6Si_2O$ (Figure 2(a)) show a dramatic change from reactants to products below 150 °C. Denoted by dotted lines, the precursors quickly react to yield NaCl and Na_2S_4 as the only observed crystalline intermediates before FeS_2 crystallizes at high temperatures. In the DSC trace in Figure 2(a), two exotherms are observed: the crystallization of NaCl at 150 °C and the crystallization of FeS_2 near 250 °C. The melting of $(C_6H_5)_6Si_2O$ is observed as the small endothermic inflection near 225 °C. The SXRD and DSC results in Figure 2(b) present the neat metathesis reaction. Here, we observe a pathway that proceeds through diffusion-limited intermediates (Na_2S_4 , Na_2S_5 , $NaFeS_2$, $Fe_{1-x}S$), which reproduces our prior work.⁷ Compared to Figure 2(a), intermediate reactions take place over a broad temperature range as compared to the abrupt change in Figure 2(a). In the DSC trace in Figure 2(b), the same exotherms are observed for NaCl and FeS_2 , yet an additional broad exotherm appears (175 °C to 225 °C) which we attribute to the crystallization of diffusion-limited intermediates. The absence of this exotherm paired with Na_2S_4 as the only identified crystalline intermediate in Figure 2(a) suggests that $(C_6H_5)_6Si_2O$ directly influences the pathway by circumventing the crystallization of diffusion-limited intermediates.

Analysis of the $(C_6H_5)_6Si_2O$ molecule *ex post facto* using ¹H NMR spectroscopy (Fig. S3) reveals that the molecule remains unchanged. The similarities between the washed 4.5 mol% $(C_6H_5)_6Si_2O$ assisted metathesis products as compared to a $(C_6H_5)_6Si_2O$ standard qualitatively supports catalytic behavior. Considering the physical properties of the molecule, the $(C_6H_5)_6Si_2O$ is hypothesized to influence the reaction pathway through three mechanisms. First, the heat released upon crystallization of NaCl has the potential to melt the molecular additive, where previous studies have observed transient temperatures of metathesis reactions in excess of 1300 °C,¹¹ whereas the melting point of hexaphenyldisiloxane is 225 °C. Second, the $(C_6H_5)_6Si_2O$ could form adducts with iron or sulfur as a Lewis base or aryl-based ligand to shuttle atoms within the reaction, similar to previous studies with triphenylphosphine.¹² Finally, the $(C_6H_5)_6Si_2O$ could form some transient, metastable intermediate that is directly related to the polarizability of the Si–O–Si moiety. In order to test these hypotheses, control reactions were performed using other small molecules with targeted functional groups or properties.

Control reactions highlight the molecular role of $(C_6H_5)_6Si_2O$ in reactions at 150 °C for 24 hours. Eicosane ($C_{20}H_{42}$ MP: 42 °C) was used as a control to identify if the metathesis reaction could proceed by increasing diffusion through a molten, non-specific

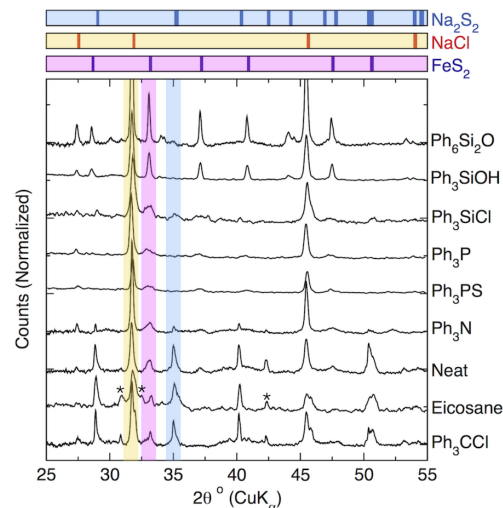


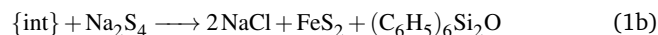
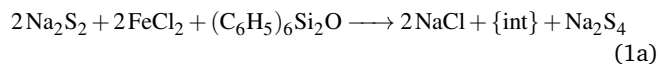
Fig. 3 PXRD results from the reaction: $Na_2S_2 + FeCl_2$ at 150 °C for 24hr with various small molecule additives. The reflections for Na_2S_2 , FeS_2 , and NaCl are shown as tick marks above and reflections are highlighted by colored rectangles for comparison. (*) denote reflections for Na_2S_4 . All concentrations are at 4.5 mol% of each molecule.

alkane; however, PXRD results in Figure 3 show limited reactivity as only NaCl, Na_2S_2 , and Na_2S_4 crystallize from the melt. Previous work on the metathetical preparation of $CuSe_2$ have shown that the Lewis base $(C_6H_5)_3P$ promotes kinetic control in the formation of the metastable pyrite polymorph by acting as a molecular shuttle for copper and selenium.¹² Therefore, triphenylphosphine ($(C_6H_5)_3P$) was added to the precursor reaction mixture at 4.5 mol% loading. The PXRD results (Fig. 3) show NaCl formation with broad, poorly resolved FeS_2 reflections. Compared to the $(C_6H_5)_6Si_2O$ addition, these results suggest Lewis base addition is not general to product formation. The lack of crystalline Fe–S phases in the diffraction pattern suggests the $(C_6H_5)_3P$ prevents FeS_2 nucleation and growth, perhaps by the same atom-transfer mechanism suggested in the $CuSe_2$ system. However, the phosphorus-sulfur bonds (BDE: 105.6 kcal/mol) are stronger than the phosphorus-selenium bonds (BDE: 86.92 kcal/mol).¹³ As such, $(C_6H_5)_3PS$ was tested, yet the PXRD results yielded similar features as $(C_6H_5)_3P$ (Fig. 3), which suggests that species that react primarily with sulfur do not yield FeS_2 . Introduction of a less basic molecule, $(C_6H_5)_3N$, also yields poorly crystalline FeS_2 , suggesting that the strength of Lewis base may not be the determining factor, either. Instead, the function of the $(C_6H_5)_6Si_2O$ seems directly related to the Si–R functional group in these metathesis reactions.

Changing the Si–R functional group changes the outcome of the reaction. Control reactions with $(C_6H_5)_3SiCl$ show reaction with Na_2S_2 , but not with $FeCl_2$ (Fig. S4), thus yielding NaCl and poorly crystalline FeS_2 (Fig. 3). Furthermore, when $(C_6H_5)_3CCl$ is used in these metathesis reactions (Fig. 3), the reaction products are similar to those without a molecule. Therefore, the formation of a thiosilane product impedes the nucleation of FeS_2 by extracting sulfur. Reactions with 13 mol% $(C_6H_5)_3SiOH$ reveals crystalline pyrite and NaCl, similar to the results using $(C_6H_5)_6Si_2O$ (Fig. 3). However, myriad control reactions show

that this results from the formation of H_2O and $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ from self-condensation reactions, as detailed in the SI.

The collective results show that $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ behaves catalytically in reducing the activation barriers in these metathesis reactions. Currently, our knowledge of *how* the $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ interacts with species present along the pathway is not well defined, yet we can hypothesize the pseudo-elementary steps to product formation based on related observations:



where an unknown intermediate, {int}, transiently stabilizes reactive iron chloride species to avoid reactions yielding diffusion limited intermediates; this intermediate is consistent with an average stoichiometry: $[(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}-(\text{FeCl})_2]$. Previous *in situ* PXRD studies of $\text{Na}_2\text{S}_2 + \text{FeCl}_2$ under air-free conditions show that reactivity is initiated by the breaking of Fe–Cl bonds.⁷ Thus, an essential attribute of our hypotheses is that the $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ aids in stabilizing the Fe–Cl species as NaCl forms. The Si–O–Si moiety possesses an unusually high bond angle ($144 \pm 0.9^\circ$) and short Si–O bond length ($1.64 \pm 0.3 \text{ \AA}$) which has been attributed to the ionic character of the Si–O bond in comparison to C–O analogs.¹⁴ This polarizability could result in cleavage of the disiloxane bonds by transition-metal halides to form transition-metal silanolates (e.g., $(\text{C}_6\text{H}_5)_3\text{SiO}-[\text{FeCl}]$ ¹⁵). Ferrosiloxanes and ferrosilicate complexed anions have also been reported that can form salts such as $\text{Na}[\text{Fe}(\text{OSiMe}_3)_4]$ ¹⁶, as well as cage-like complexes with iron.⁹ Siloxanes have also been shown to stabilize cubane-type clusters of $[\text{Fe}_3\text{S}_4]^+$ ¹⁷, which have a local structure reminiscent of the amorphous Fe-S intermediate we previously reported in water-promoted metathesis reactions.⁷ Another plausible hypothesis is that $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ may complex the iron(II) chloride through cation- π interactions. As the siloxane functional group is quite sterically hindered, we may be observing a haptic-type interaction where the intermediate iron-containing species is stabilized through interaction with phenyl groups as chloride anions are removed to form NaCl. Interestingly, the phenyl groups in these disiloxane molecules can exhibit significant dipole moments along the $(\text{C}_6\text{H}_5)-\text{Si}-\text{O}$ bond ($p \rightarrow d$) π .¹⁸ The electron withdrawal from the phenyl groups could hypothetically provide a haptic bonding environment, where a half-sandwich type complex could form. The Si–O bond polarization would explain why $(\text{C}_6\text{H}_5)_3\text{SiCl}$ or $(\text{C}_6\text{H}_5)_3\text{CCl}$ are not as reactive. This type of coordination complex would explain the absence of crystalline inorganic intermediates containing iron or molecular intermediates. As occurs oftentimes in molecular catalysis, we cannot identify the true intermediate due to its short lifetime or metastability at 150 °C. In reactions without $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$, iron chloride species will react to yield diffusion-limited intermediates (e.g., NaFeS_2 , Fe_{1-x}S), which suggests diffusion of reactants or intermediates to a reaction interface is slower than the lifetime of the iron chloride species. By coordinating these iron chloride species, their lifetime

is extended to permit nucleation of FeS_2 directly at low temperatures. The proposed pseudo-elementary steps in Equations 1a and 1b suggest complete conversion to FeS_2 , yet the results in Figure 1 suggest a portion of the products may be amorphous or poorly crystalline. Thus, we cannot eliminate the hypothesis that some of the iron and sulfur is consumed in a pathway that involves an amorphous Fe-S phase as previously observed in a related system.⁷

This communication demonstrates that organosilicon molecules change the reaction pathway in the metathetical preparation of FeS_2 at low temperatures (150 °C). Addition of $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ has a catalytic effect on the formation of FeS_2 over a narrow range in concentration (2-5 mol%). Analysis of the reaction pathway with $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ reveals a decrease in the number of diffusion-limited crystalline intermediates. We hypothesize that $(\text{C}_6\text{H}_5)_6\text{Si}_2\text{O}$ catalyzes the reaction pathway by stabilizing reactive iron chloride species either through a cleavage of the Si–O bond or through a haptic coordination between iron and phenyl R-groups. This contribution identifies strategies for rationally designing solid-state reactions at low-temperature by coordinating functional molecules with specific reactant compositions.

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Conflicts of interest

There are no conflicts to declare.

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