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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: FeCl₂ + $Na_2S_2 \rightarrow 2NaCl + FeS_2$. Specifically, hexaphenyldisiloxane ((C₆H₅)₆Si₂O) 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 (C₆H₅)₆Si₂O. 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 (C₆H₅)₆Si₂O 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 synthesis 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 (CH₃)₃Si-(S/Se) and trioctylphosphine to coordinate and transfer atoms into specific lattice sites.^{3,4} For solidstate synthesis, reactions must proceed at temperatures where

these molecules do not decompose in order to take advantage of their targeted functional groups.

Exchange reactions, including metathesis, provide lowtemperature solid-state syntheses where reaction kinetics can be controlled using small molecules to direct product selectivity. For example, the addition of molecules like H_2O and $(C_6H_5)_3P$ 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 $CuSe_2$ 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.

In this work, we study a metathesis reaction $(Na_2S_2 + FeCl_2 \rightarrow FeS_2 + 2NaCl)$ that produces pyrite FeS₂ 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 $H_2O(g)$ 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 transfer,⁸ ferrosiloxane adducts,⁹ Table S1, ESI⁺) when changing the Si-X (Si-O-Si, Si-OH, Si-Cl) functional group. We demonstrate that the addition of (C₆H₅)₆Si₂O to inorganic precursors selectively yields crystalline NaCl and FeS2 at low concentrations and reaction times. Hexaphenyldisiloxane, a weak Lewis base, appears to catalytically lower the energy barrier to formation of FeS₂. Varying the concentration of $(C_6H_5)_6Si_2O$ 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 (SXRD) and differential scanning calorimetry reveals that (C6H5)6Si2O 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

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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 (C₆H₅)₆Si₂O yields FeS₂ in metathesis reactions performed at temperatures that are significantly lower than for the neat reaction. PXRD data in Fig. S1 (ESI⁺) of the neat metathesis reaction show formation of crystalline NaCl, small amounts of pyrite FeS₂, along with high amounts of unreacted Na₂S₂ precursor (Table S2, ESI⁺). As compared to the metathesis reaction without a molecular additive, the PXRD results using 4.5 mol% $(C_6H_5)_6Si_2O$ (MP: 225 °C) show an increase in the crystallinity and phase fraction of FeS₂ and NaCl (\sim 4:1 NaCl: FeS₂ in Fig. S1, ESI⁺). After 24 h at 150 °C, the reaction has not proceeded to completion (*i.e.*, 2:1 NaCl: FeS₂ in Fig. 1), yet longer reaction times (>24 h) yield more FeS₂, suggesting that growth of FeS₂ is still limiting the reaction at 150 °C. Nonetheless, as the (C₆H₅)₆Si₂O concentration increases from 0.5 mol% to 4.5 mol%, the mol% phase fraction of the FeS₂ in the PXRD results increases (Table S2, ESI⁺ and Fig. 1). At higher mol% concentrations ($x \ge 4.5$ mol%), the products are comprised of Na₂S₂ and Na₂S₄. At 0.5 mol% (C₆H₅)₆Si₂O, 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 Fe₇S₈ but no FeS₂ supporting previous studies of highly exergonic metathesis reactions, such as $MoCl_5 + 5/2Na_2S$, where similar disproportionation of alkali sulfides results in decomposition of sulfide anions to sulfur.^{10,11} Taken together, these observations indicate that (C₆H₅)₆Si₂O directly influences the pathway and the reaction rate.

The decrease in reactivity at higher molecular loadings ($x \ge$ 4.5 mol%) is explained by the relative volume fractions, which results in a decrease in physical contact between precursors. For



Fig. 1 Mole fraction of crystalline products from Rietveld refinements of PXRD data when varying the mol% concentration of $(C_6H_5)_6Si_2O$ in metathesis reactions at 150 °C for 24 h. The inset shows an intact reaction pellet when using 4.5 mol% $(C_6H_5)_6Si_2O$ as compared to the reaction with 0.5 mol% $(C_6H_5)_6Si_2O$. At 0.5 mol% $(C_6H_5)_6Si_2O$, the pellet disintegrated from a rapid propagation event leaving condensed sulfur.

perspective, 8.5 mol% $(C_6H_5)_6Si_2O$ 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 ($0.5 < x \le 4.5 \text{ mol}\%$), the (C_6H_5)₆Si₂O 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)₆Si₂O do not propagate, which results in higher yields of FeS₂.

Temperature-dependent in situ synchrotron X-ray diffraction experiments reveal that (C₆H₅)₆Si₂O reduces the number of crystalline intermediates observed along the reaction pathway. Fig. 2 presents combined in situ SXRD and differential scanning calorimetry (DSC) experiments heated at 10 °C min⁻¹ to 300 °C. Metathesis reactions with 4.5 mol% $(C_6H_5)_6Si_2O$ (Fig. 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 Na₂S₄ as the only observed crystalline intermediates before FeS₂ crystallizes at high temperatures. In the DSC trace in Fig. 2(a), two exotherms are observed: the crystallization of NaCl at 150 °C and the crystallization of FeS2 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 Fig. 2(b) present the neat metathesis reaction. Here, we observe a pathway that proceeds through diffusion-limited intermediates (Na2S4, Na2S5, NaFeS2, $Fe_{1-x}S$, which reproduces our prior work.⁷ Compared to Fig. 2(a), intermediate reactions take place over a broad temperature range as compared to the abrupt change in Fig. 2(a). In the DSC trace in Fig. 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 Na₂S₄ as the only identified crystalline intermediate in Fig. 2(a) suggests that (C₆H₅)₆Si₂O directly influences the pathway by circumventing the crystallization of diffusion-limited intermediates.

Analysis of the (C₆H₅)₆Si₂O molecule ex post facto using ¹H NMR spectroscopy (Fig. S3, ESI⁺) reveals that the molecule remains unchanged. The similarities between the washed 4.5 mol% (C₆H₅)₆Si₂O assisted metathesis products as compared to a (C₆H₅)₆Si₂O 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 (C₆H₅)₆Si₂O 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 (C₆H₅)₆Si₂O 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.



Fig. 2 In situ SXRD results of the reaction $Na_2S_2 + FeCl_2$ using (a) 4.5 mol% (C_6H_5)₆Si₂O and (b) with no molecular additive heating at 10 °C min⁻¹ 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.

Control reactions highlight the molecular role of (C₆H₅)₆Si₂O in reactions at 150 °C for 24 hours. Eicosane (C20H42 MP: 42 °C) was used as a control to identify if the metathesis reaction could proceed by increasing diffusion through a molten, non-specific alkane; however, PXRD results in Fig. 3 show limited reactivity as only NaCl, Na₂S₂, and Na₂S₄ crystallize from the melt. Previous work on the metathetical preparation of CuSe₂ 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 ((C₆H₅)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 FeS₂ reflections. Compared to the (C₆H₅)₆Si₂O 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 FeS₂ nucleation and growth, perhaps by the same atom-transfer mechanism suggested in the CuSe₂ system. However, the phosphorus-sulfur bonds (BDE: 105.6 kcal mol^{-1}) are stronger than the phosphorus-selenium bonds (BDE: 86.92 kcal mol⁻¹).¹³ As such, (C₆H₅)₃PS was tested, yet the PXRD results yielded similar features as (C₆H₅)₃P (Fig. 3), which suggests that species that react primarily with sulfur do not yield FeS₂. Introduction of a less basic molecule, (C₆H₅)₃N, also yields poorly crystalline FeS₂, suggesting that the strength of Lewis base may not be the determining factor, either. Instead, the function of the (C₆H₅)₆Si₂O 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 $(C_6H_5)_3$ SiCl show reaction with



Fig. 3 PXRD results from the reaction: $Na_2S_2 + FeCl_2$ at 150 °C for 24 h with various small molecule additives. The reflections for Na_2S_2 , FeS₂, 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.

 Na_2S_2 , but not with FeCl₂ (Fig. S4, ESI[†]), thus yielding NaCl and poorly crystalline FeS₂ (Fig. 3). Furthermore, when $(C_6H_5)_3$ CCl 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 FeS₂ 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 H₂O and $(C_6H_5)_6Si_2O$ from self-condensation reactions, as detailed in the ESI.[†]

The collective results show that $(C_6H_5)_6Si_2O$ behaves catalytically in reducing the activation barriers in these metathesis reactions. Currently, our knowledge of how the $(C_6H_5)_6Si_2O$ 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:

 $2Na_2S_2 + 2FeCl_2 + (C_6H_5)_6Si_2O \rightarrow 2NaCl + \{int\} + Na_2S_4 \quad (1a)$

$$\{int\} + Na_2S_4 \rightarrow 2NaCl + FeS_2 + (C_6H_5)_6Si_2O \quad (1b)$$

where an unknown intermediate, {int}, transiently stabilizes reactive iron chloride species to avoid reactions vielding diffusion limited intermediates; this intermediate is consistent with an average stoichiometry: [(C₆H₅)₆Si₂O-(FeCl)₂]. Previous in situ PXRD studies of Na₂S₂ + FeCl₂ 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 (C₆H₅)₆Si₂O aids in stabilizing the Fe-Cl species as NaCl forms. The Si-O-Si moiety possesses an unusually high bond angle (144 $^{\circ} \pm 0.9^{\circ}$) and short Si–O bond length (1.64 \pm 0.3 Å) 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., $(C_6H_5)_3$ SiO-[FeCl]¹⁵). Ferrosiloxanes and ferrosiliconate complexed anions have also been reported that can form salts such as Na[Fe(OSiMe₃)₄],¹⁶ as well as cage-like complexes with iron.⁹ Siloxanes have also been shown to stabilize cubane-type clusters of $[Fe_3S_4]^+$, which have a local structure reminiscent of the amorphous Fe-S intermediate we previously reported in waterpromoted metathesis reactions.⁷ Another plausible hypothesis is that $(C_6H_5)_6Si_2O$ 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 (C6H5)-Si-O bond $((p \rightarrow d)_{\pi})$.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 (C₆H₅)₃SiCl or (C₆H₅)₃CCl 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 $(C_6H_5)_6Si_2O_7$ iron chloride species will react to yield diffusion-limited intermediates (e.g., NaFeS₂, 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 FeS₂

directly at low temperatures. The proposed pseudo-elementary steps in eqn (1a) and (1b) suggest complete conversion to FeS_2 , yet the results in Fig. 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 FeS₂ at low temperatures (150 °C). Addition of $(C_6H_5)_6Si_2O$ has a catalytic effect on the formation of FeS₂ over a narrow range in concentration (2–5 mol%). Analysis of the reaction pathway with $(C_6H_5)_6Si_2O$ reveals a decrease in the number of diffusion-limited crystalline intermediates. We hypothesize that $(C_6H_5)_6Si_2O$ 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 solidstate 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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