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Gallium-catalyzed Boron-assisted Recycling of Any Silicone Waste: Depolymerization to produce Chlorosilanes as key industrial commodities

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20 **Abstract:** Chemical recycling back to monomers is a key strategy for a sustainable circular polymer economy. Silicone polymers and networks are wonder hybrid materials with a robust inorganic backbone and tunable organic substituents tailored for various daily life applications. However, their recycling, including mechanical and chemical processes, remains at its infancy.
25 We present a generalized method to depolymerize, at ambient temperatures, any silicone waste; including a very wide range of silicone-based materials and post-consumer waste *a.k.a.* end-of-life crosslinked polydimethylsiloxane-based networks within formulated materials. The reaction harnesses an efficient gallium catalyst, with a 30-million-fold rate enhancement, and boron trichloride as source of chloride to produce nearly quantitative yields of (methyl)chlorosilanes
30 *a.k.a.* key intermediates from the Müller-Rochow process, at the cornerstone of the Si industry.

One-Sentence Summary:

Chemical recycling of any silicone waste harnessing BCl₃ and Ga catalysis produces key industrial chlorosilanes.

CONTEXT/RATIONALE

Silicone polymers are ubiquitous materials in our daily lives owing to their exceptional mechanical and thermal stability, chemical resistance and low toxicity that are advantageous in various applications such as household, automotive, medicinal care, etc (1). In 2022, the world production of silicone polymers reached >8 million tons, representing a market value at ~20 billion USD (2). Due to its upstream hydrometallurgical process step, the production of silicones is energy intensive. The metallurgy to reach Si metal (relying on the mining of quartz) and to a lesser extent the Müller-Rochow process to yield chlorosilanes both represent >70% of CO₂ footprint of silicones. They are the most energy-intensive steps of the silicone industry and circumventing them is appealing. Silicones recycling thus appears as a key solution to conserve already depleting resources (such as quartz) and minimize energy consumption.

The current solution for discarding silicone waste (oils + elastomers with and without fillers) is mostly to either incinerate or landfill. Although silicone wastes have so far been considered mostly benign for our environment (eventual degradation in soil to CO₂, H₂O and SiO₂), *do nothing and let it accumulate and slowly degrade over the next thousand years* would be an unsatisfactory and inefficient solution for the end-of-life of these materials. In addition, some silicone-based compounds have recently come under scrutiny, fostering novel strategies such as eco-design for silicones (3) and biocatalytic pathways to deal with volatile methylsiloxanes (4). Addressing silicone waste is thus crucial to a sustainable future for our environment and society, aiming at circularity for polymers. Unlike some specific thermoplastics such as PET or Polyolefins (5-8), whose recycling are widely developed — mechanical in particular (9), but more recently chemical (10-14) — the recycling of silicone-based polymers is underexploited and few examples exist (15). Chemical recycling could prove particularly efficient for silicones since it sidesteps the power-hungry metallurgy and Müller-Rochow processes. According to the studies from Elkem Silicones©, the chemical recycling of silicone wastes can reduce 65% of energy consumption and 75% in greenhouse emission (16,17). Developing novel processes toward recycling and circularity of silicone polymers is thus highly desirable.

A main reason for the difficult chemical recycling of silicone materials and particularly elastomers (crosslinked networks) is their sophisticated multi-component silicone-based formulations. Those elastomers/rubbers often exist as a mixture of crosslinked polysiloxanes, inorganic and organic fillers, technical additives, and catalysts (15). Since they are cured or crosslinked in the presence of catalyst, they can no longer be melted or reshaped. Therefore, mechanical recycling will warrant downcycling as rubber powder or crumbs and thus has rather limited applications. Consequently, chemical upcycling to recover key industrial intermediates (15,16) appears as a seducing and likely alternative for complex silicone waste.

The chemical recycling of waste silicones has nonetheless been studied for a long time, yet mainly focusing on the conversion of silicone polymers to cyclosiloxanes (**method 1**, cyclic monomers, *see Fig. 1*). Very rarely has “upcycling” to halogenated organosilanes been considered as efficient strategy for chemical recycling (**method 2**, Cl-based monomers, *see Fig. 1*). Both cyclosiloxanes and halogenated organosilanes are key intermediates of the silicone industry (*see Fig. 1*).

On the one hand (**method 1**), a strong alkaline base/complex or fluorine derivatives could be used as the efficient catalyst (generation of propagating silanolate) for the deconstruction of silicone polydimethylsiloxane (PDMS) chains to cyclosiloxanes through back-biting successive nucleophilic attacks (16, 18-20). This is a desirable short recycling loop: “back-to-cyclic

monomers”. We recently provided a straightforward strategy for several silicone wastes: a “back-to-cyclics” methodology with a very efficient, readily available and recyclable catalyst (16). However, the strategy lacks universality and tolerance towards high contents of moieties supporting Si-H bonds. More detrimentally, it cannot properly handle formulated elastomers and highly crosslinked resins which account for a large fraction of all silicone waste (> 40%), especially present in post-consumer waste.

On the other hand, analogue to **method 2** but for fluorosilanes, the conversion of silicone polymer to Si-F products is a thermodynamically favored chemical route. Enthaler *et al.* have presented a new synthetic method for the depolymerization of silicone oils/elastomers to produce the corresponding fluorosilanes (21). An excess of benzoyl fluoride was used as the fluorine sources and the reaction often proceeds in the presence of a Zinc catalyst at elevated temperatures (120-190°C). However, the drawback of this method is twofold: it involves the price/availability/lack of atom-economy of fluorine/fluoride sources and the release of some volatile and hazardous fluorosilanes during “recycling”. Moreover, utilization of those fluorosilanes is rather limited industrially and is “outside the loop” of silicon/silicone main industrial train.

Chlorosilanes (**method 2**) are the most important intermediates in silicone industrial production. They are conventionally produced through Müller-Rochow process that involves a copper-catalyzed reaction of methyl chloride and metallurgic silicon in a fluidized bed reaction (300°C, 2-5 bar) (22). However, the chemical recycling of silicone polymers to (methyl)chlorosilanes is seldom reported due to unfavored thermodynamic of Si-Cl bond in comparison to Si-O featured in silicone backbones (23). There is only one report by Enthaler *et al.*, mentioning the conversion of silicone oils to chlorosilanes (24). However, reaction conditions (high catalyst loading [Fe], excess of unsustainable acyl chloride, high temperature ~ 190°C) and narrow scope with waning reactivity have limited its application in silicone recycling. Alternatively, we provide a *chew-all-waste* chemical recycling strategy based on an inorganic chloride source, boron trichloride, whose side-product boron oxide B₂O₃ can be used by the borosilicate glass industry or looped back into boron trichloride (25,26).

Herein, we present an effective method for depolymerization of any silicone polymers – including functional oils, block copolymers or end-of-life/industrial elastomers and filled crosslinked materials waste – to produce (methyl)chlorosilanes as key commodities of the silicone industry. The reaction is performed at ambient temperature in the presence of low metal catalysts (typically 0.5 mol% down to 0.02 mol%, *i.e.* from 0.005 equiv. down to 0.0002 equiv. of Si-O bonds) using boron trichloride as a depolymerizing reagent. The heterobimetallic ion pairs resulting from Si-O-Si bond, and BCl₃ (as Lewis acid and source of Cl) and GaCl₃ (as a catalyst) promoted Si-O and B-Cl scrambling from BCl₃ and Si-O-Si silicone backbone. Among various Lewis acids, GaCl₃ exhibited superior performances as a catalyst, but not as a chloride source when compared to far superior BCl₃ (see below). The [BCl₃•GaCl₃] combination in the presence of Si-O-Si based backbone can yield up to 99% chlorosilanes. Even if this type of Lewis acidic behavior is not extensively documented (see dedicated section in ESI: “Precedent literatures on homo/hetero-bimetallic reactivity”), multi-nuclear NMR spectra of the active species elucidate and confirm prior findings. With the support of molecular modelling performed at the DFT level, we unveil the atypical mechanism of this depolymerization reaction.

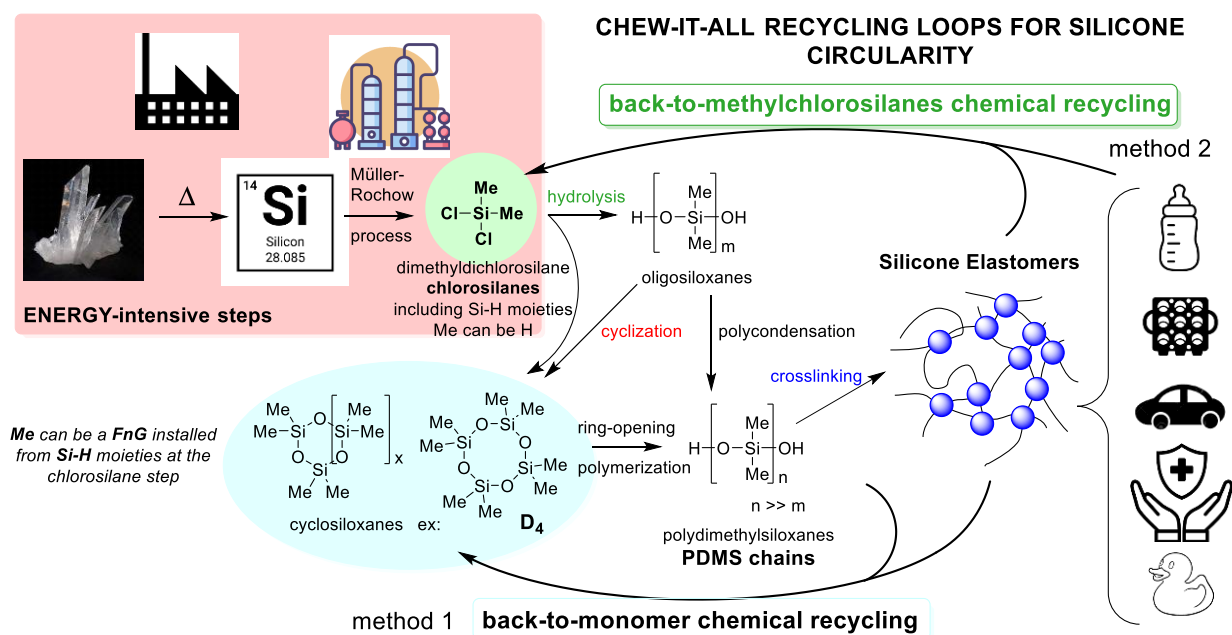


Fig. 1. General strategies for the chemical recycling of silicone polymers.

RESULTS & DISCUSSION

The depolymerization of silicone polymers was first studied at 40°C during 24 hours using a solution of boron chloride in dichloromethane (1M) as a source of chloride. BCl_3 was selected to counterbalance the thermodynamically disfavored formation of Si-Cl bonds from Si-O bonds. Silicone oil **1** (MD₇₀M, $M_n=5340 \text{ g mol}^{-1}$, viscosity 100 cSt) was used as a model substrate. First, the Si-O-Si backbone cleavage was evidenced using BCl_3 in the absence of catalyst (*see* entry 1, **Table 1**). Some Si-O bond cleavage was observed along with the formation of Si-Cl bonds through the formation of products **4**, but no volatile (methyl)chlorosilanes **2** and **3** could be evidenced. To favor the chlorination process, catalysis by a Lewis acid was then evaluated. Combination of BCl_3 with another Lewis acid seemed promising to enhance reactivity and Si-O bond cleavage.

Heterobimetallic reactivity was first discovered decades ago but its application through the combination of two Lewis acidic molecules is scarcely reported. One key example was reported by Sugasawa, using stoichiometric amount of BCl_3 and GaCl_3 , to realize a specific *ortho*-substitution acylation of aniline derivatives (27). This concept was later exploited by Negishi to understand what governs or induces the ate complexation, transmetallation or dynamic polarization (*see* **Fig. S6** and more generally the “Precedent literatures on homo/hetero-bimetallic reactivity” discussion in ESI), concluding that the new metal center in the putative heterobimetallic complex must be more electrophilic than the original “non-activated” one (28). Recently, Schindler *et al.* have found that the hetero-bimetallic species, harnessing Fe and Al Lewis acid character, could be used as excellent catalyst for carbonyl-olefin ring-closing metathesis (29,30). Interestingly, these reports reinforce the idea that the super-electrophilic character arising from such species can unlock some unconventional reactions. Although the experimental data were meticulously interpreted by a computed mechanism, spectroscopy studies did not reveal any conclusive evidence of active species. More recently, Klare, Oestreich *et al.* reported a new halodealkylation of alkylsilanes, harnessing the super-electrophilic character of arenium cations and corresponding chlorenium/silylium intermediates (31,32). The main goal here

is to unlock a valuable, yet thermodynamically unfavorable, formation Si-Cl bond from Si-O bonds. We tried to capitalize on the hetero-bimetallic [BCl₃•Lewis acidic catalyst] combination to induce chlorosilanes formation from Si-O-Si backbones.

To that effect, a wide range of *Lewis acids* (MCl_x, 0.5 mol% of siloxane unit) were tested as catalysts for the depolymerization reaction (*see Table 1*, entries 2 to 9). On the one hand, no reactivity was observed using ZnCl₂, MnCl₂, CoCl₂ whereas dichlorodimethylsilane **2** was obtained in low yield (12%) in the presence of FeCl₂. Interestingly, the depolymerization with FeCl₃ gave an excellent yield of **2** (up to 97%), albeit after 24 hours. On the other hand, the reaction using AlCl₃ or GaCl₃ provided an excellent reactivity in a shorter timeframe. The chlorosilane **2** was obtained in 85% and 98% yield respectively, after only 30 minutes. We hypothesized that the increased chlorophilicity of these Lewis acids leads to the formation of super-electrophile reagent [O-BCl₂⁺] from BCl₃ with coordination of Si-O-Si behaving as the Lewis base and GaCl₃ harvesting the Cl⁻ to generate the favorable [GaCl₄⁻] anion, thus promoting the cleavage of Si-O-Si bonds (*see discussion about the mechanism in a following dedicated section*). Moreover, (Me₃SiO)-functionalized chain-ends could for instance be recovered with this process as corresponding functionalized chlorosilanes (Me₃SiCl, 99% yields). Furthermore, other gallium pre-catalyst species were also evaluated for depolymerization reaction. The reactions with GaBr₃ and Ga(OTf)₃ gave 95% and 70% of **2** while no desired product was observed when Ga₂O₃ was employed as a catalyst precursor, likely due to immiscibility issues. In the Ga-based series, GaCl₃ was thus selected for further investigation, including temperature effect and catalyst loading on the performances of the depolymerization reaction (*Table S1*). Lowering the temperature down to 0°C or 25°C resulted in a good but non-quantitative yield of **2** obtained in 67-70% along with the formation of silyl ether product **3** (10-11% yield). When the catalyst loading was decreased further down to 0.02 mol%, the reaction time had to be consequently increased to achieve complete depolymerization reaction. Considering all these factors, GaCl₃ (0.5 mol%, 40°C) was chosen for further investigation, in particular, concerning the choice of solvent or diluent (swelling in the case of crosslinked materials).

Solvent. We verified that our depolymerizing strategy did not rely on the use of dichloromethane (DCM) as a solvent. Alternative valuable solvents, either for the dilution (linear PDMS waste) or for the necessary swelling of any silicone waste (including mixed elastomers), such as toluene and heptane, have been investigated (*see entries 10 & 11, Table 1*). Since BCl₃ has a low boiling point (12°C) and it is hard to handle in a neat state, its solution in different solvent (CH₂Cl₂, heptane or toluene) was first evaluated for this reaction. When the reaction was performed at 40°C for 30 minutes, the depolymerization in DCM yielded 98% of **2**, while utilizing BCl₃ in *n*-heptane or toluene solutions provided yields of **2** at 60% and 62%, respectively. More interestingly, when the reaction's time was increased, a better conversion of **1** was also observed. After 2 hours, the depolymerization in toluene gave an excellent dichlorosilane yield (95%) while the depolymerization in *n*-heptane provided 75% yield of **2** after 5 hours. Furthermore, the temperature could also be increased when higher boiling-point toluene was used. After 1 hour at 90°C, nearly quantitative yield of **2** was obtained with very little percentage of silyl ether **3**. Thus, both more sustainable and friendly solvents provided good to excellent yields of desired (methyl)chlorosilanes, albeit using slightly longer reaction times (*see entries 10 & 11, Table 1*).

Table 1. Catalysts and reagent screening for depolymerization of model substrate.

$$\text{Me}_3\text{SiO}-\left(\text{Si}(\text{CH}_3)_2\text{O}\right)_n-\text{Si}(\text{CH}_3)_2\text{Cl} + \text{BCl}_3 \xrightarrow[40^\circ\text{C}]{\text{Catalyst (0.5 mol\%)}} \text{Me}_2\text{SiCl}_2 + (\text{Me}_2\text{SiCl})_2\text{O} + \text{Cl}-\left(\text{Si}(\text{CH}_3)_2\text{O}\right)_n-\text{Si}(\text{CH}_3)_2\text{Cl} + \text{Me}_3\text{SiCl} + \text{B}_2\text{O}_3$$

1 2.2 equiv. of Cl⁻ per Si-O units 2 3 4 or 5 6

Entry	Conditions ^a	Yield of 2 ^b	Yield of 3 ^b	Yield of 4 ^b	Yield of 5 ^c
1	No catalyst, 24h	0	0	100	22
2	ZnCl ₂ or CoCl ₂ or MnCl ₂ (0.5), 24h	0	0	100	20-44
3	FeCl ₂ (0.5), 24h	12	15	77	99
4	FeCl ₃ (0.5), 24h	97	3	0	99
5	AlCl ₃ (0.5), 0.5h	85	12	3	99
6	GaCl ₃ (0.5), 0.5h	98	2	0	99
7	GaBr ₃ (0.5), 0.5h	95	5	0	99
8	Ga(OTf) ₃ (0.5), 0.5h	70	9	21	99
9	Ga ₂ O ₃ (0.5), 24 h	0	0	100	20
10	BCl ₃ in <i>n</i> -heptane, 0.5h (5h)	60(75)	24(16)	16(9)	99(99)
11	BCl ₃ in toluene, 0.5h (2h)	62(95)	17(5)	21(0)	99(99)

^a Reaction conditions: silicone oil **1** (300 mg, 4 mmol Si-O), catalyst, BCl₃ in dichloromethane 1M (3 mL, 9 mmol Cl⁻, 2.2 equiv. of siloxane units). ^b Yield of chlorosilanes **2**, **3**, **4** were determined by ¹H-NMR analyse using mesitylene as an internal standard. ^c Yield of **5** was calculated by the ratio between the amount of TMS-Cl we observed through cleavage and the amount of trimethylsilyl in starting material: this thus corresponds to recovery of chain ends and should be treated as a separate yield.

Since the BCl₃/GaCl₃ proved to be a powerful combination for the transformation, we wanted to verify that other potentially industry-compliant chloride sources could be utilized.

Source of chloride. AlCl₃ was tested as an alternative chloride source for the depolymerization as previously reported by Mair *et al.* (33) (**Table S2**). Of note: AlCl₃ is a byproduct of the Si industry (after the Müller-Rochow & subsequent hydrolysis processes). The reaction was carried out at different temperatures (40°C for CH₂Cl₂, 90°C for ClCH₂CH₂Cl as solvents/swelling agents) for 24 hours. However, only low yield of chlorosilane **2** (10-12%) was observed. We suspect that if the first Al-Cl bond of AlCl₃ is reactive, the subsequent -O-AlCl₂ and further oxygenated counterparts are far less efficient chlorinating reagents. Additionally, GaCl₃ was ruled out as the chlorinating reagents, due to its favored transmethylation (34). Finally, other metallic or metalloid-based chloride sources such as TiCl₄, SiCl₄, CuCl₂ or even a solution of HCl in dioxane (4M) were also used as alternative chloride sources but no reactivity was detected in all these cases (**Table S2**), highlighting the advantageous role of boron chloride as a source of chloride.

Recycling functional waste oils. After optimization with PDMS oil **1** with viscosity of 100 cSt, the conditions for the depolymerization of other silicone waste were selected as follow: BCl₃ as Cl source (2.2 eq. of Cl per Si atom to convert, mainly targeting Me₂SiCl₂ as product, which corresponds to 1.1 eq. of B-Cl bond per Si-O bond, cat: GaCl₃ (0.5 mol%), 40°C for 30 min. We applied these conditions to a series of silicone oils with different chain-end functionalities (**Fig. 2** and **Table S3**). First, several trimethylsilyl end-capped polysiloxanes with higher viscosities **7** and **8** (respectively 1000 cSt and 10⁶ cSt) were examined. Interestingly, all of them gave an excellent

yield of chlorosilane **2** (95-97%) upon recycling, indicating that the molar masses of the linear PDMS or silicone gum (very high molar-mass linear PDMS) do not affect the efficiency of the depolymerization method. Then, the vinyl-terminated silicone oils **9** and **10** were also tested under standard conditions. A good yield of **2** (93-96%) was also afforded. Additionally, silanol-terminated polysiloxanes **11** and **12** were also investigated, giving the desired product **2** in very good yields (93-97%). Moreover, the resin **13**, which consists of 75% of D moieties, 20% of T moieties and 4% of M moieties, was tested under reaction condition (35). Interestingly, 90% of **2** and 10% of **3** were obtained after the deconstruction. Besides, some advantageous depolymerization products of T fraction such as MeSiCl₃ and (MeSiCl₂)₂O were detected for the first time in 10% and 50% yield respectively. T moieties are particularly challenging for silicone recycling since their accumulation in many “back-to-cyclics” depolymerization strategies often yields a crosslinked insoluble fraction that requires process discontinuity and extensive cleaning (15, and see discussion on demethylation in ref.16 in particular).

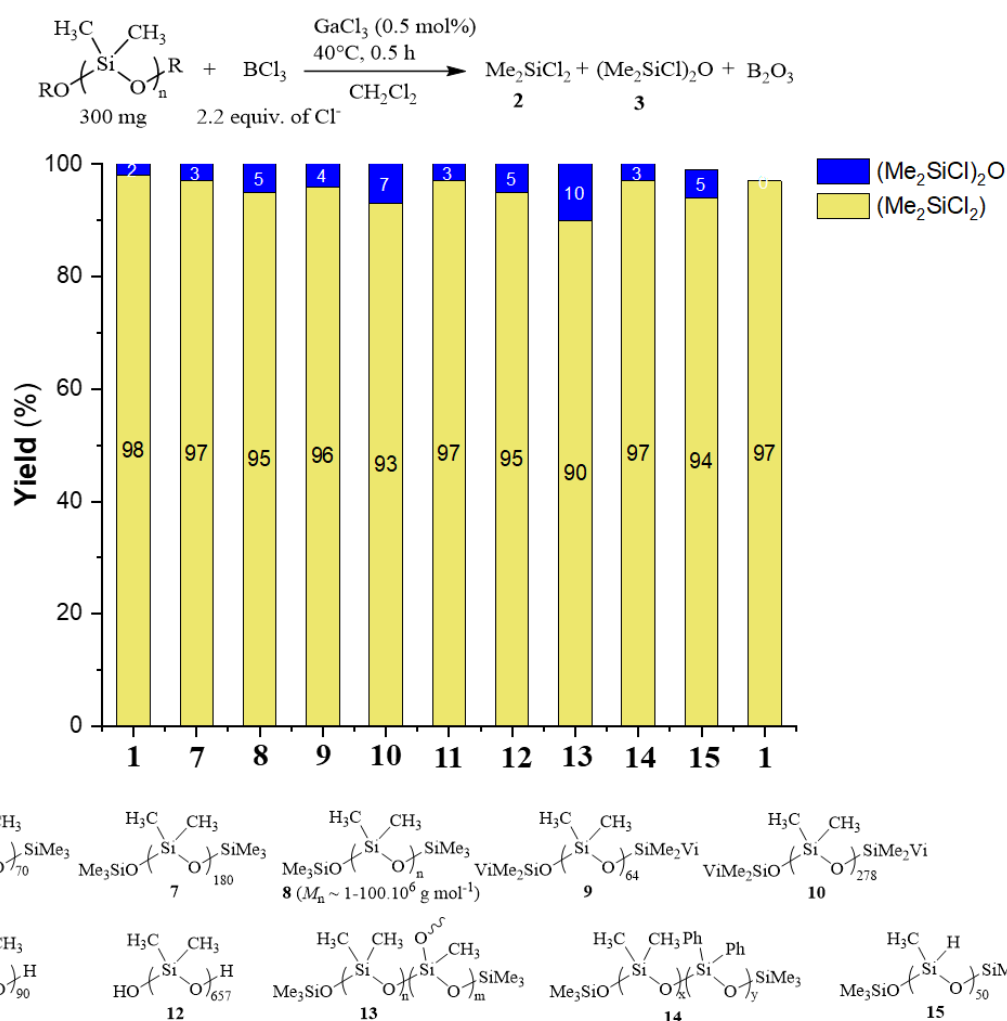


Fig. 2. Scope for the chemical recycling of silicone oils/copolymer to corresponding chlorosilanes. ^aMeSiCl₃ (10% yield) and (MeSiCl₂)₂O (50% yield) were observed as the depolymerisation of T unit; ^bobserved corresponding chlorosilanes are Me(H)SiCl₂ and (Me(H)SiCl)₂O; ^cscale-up experiment for 2 g of **1**.

Furthermore, and to showcase the robustness and universality of the method, waste silicone block copolymers **14** which has phenyl content (5 mol%) and a viscosity of 60000 cSt, was also investigated under optimized depolymerization conditions. After 30 minutes, chlorosilane **2** could be afforded in a yield of 97% based on D moieties (36). Eventually, silicone oil **15** containing numerous Si-H moieties, extremely challenging to recycle compared to fully methylated silicone oils regarding both safety and chemical instability, was evaluated for the depolymerization. Excellent yields of methyldichlorosilane (Me(H)SiCl₂) (> 95%) and minor silyl ether (Me(H)SiCl)₂O (< 5%) were observed. In all examples, chain-end-derived chlorosilanes (M moieties) were recovered almost quantitatively (see grey column for product **5**, separated with doubled line in Table S3, ESI), except for silanol-terminated substrates depolymerization, logically lost during chlorination. These chain blockers are particularly valuable to the *Si* industry.

Scale-up. Finally, a scale-up of the method was conducted using first 2 g of silicone oil **1** and then ~ 80 g of **1** (see scale-up section in ESI) in a dedicated semi-batch process. A distillation setup was applied to separate the volatile fraction (containing Me₂SiCl₂ and CH₂Cl₂) and solid co-product (B₂O₃). The side-product was analyzed by solid-state ¹¹B NMR spectroscopy and is mainly comprised of the boron oxide with some B-Cl residual bonds. Interestingly, chlorosilane **2** was observed in a high yield of 97% whereas boron oxide was also isolated as a white solid (95% yield) for the 2 g scale, and in 95-97% (D moieties in liquid distillate plus leftovers in boiler) and ~99% respectively for the promising 80 g-scale experiment (see ESI for details). This latter experiment allowed for a monitoring of the depolymerization reaction (see ESI section dedicated to scale-up), which is exploited in the mechanism investigation following section. Additionally, we could achieve a more precise characterization of the B₂O₃ co-product from this larger scale, showing minimal contamination by B-Cl bonds, likely due to the slight excess used to warrant full transformation to chlorosilanes (ESI, *Fig. S54 & S55*). This side product of chemical recycling could therefore be recycled in another industrial loop (37) or reused by the borosilicate glass industry.

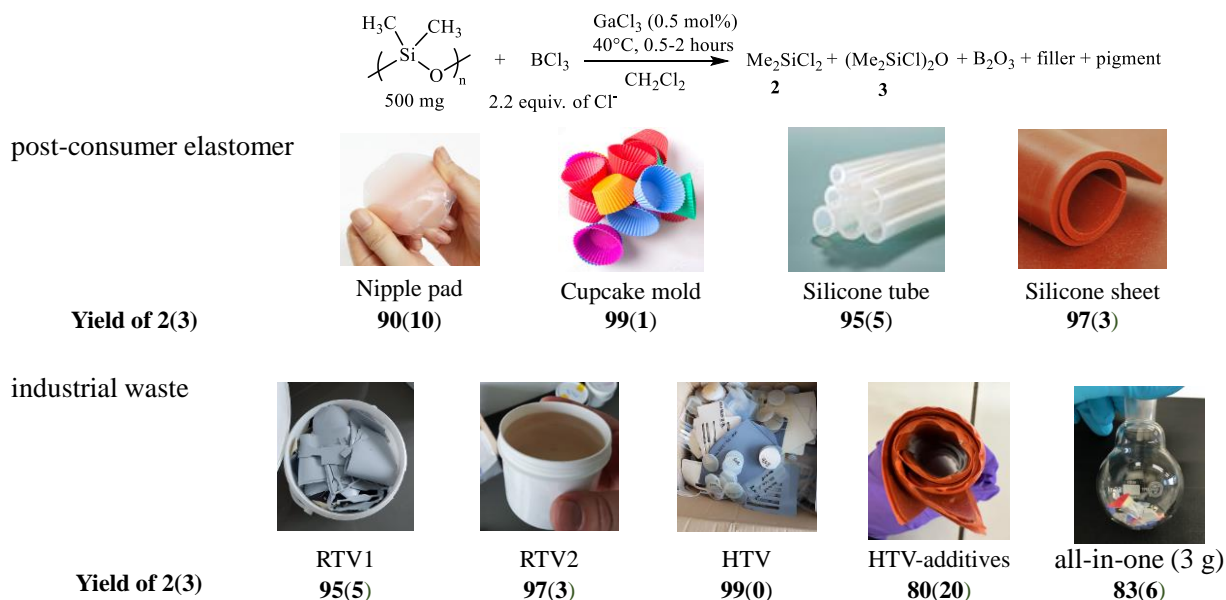
These scale-up experiments confirm the first selective and scalable method to convert silicone oils into valuable chlorosilanes, paving the way towards industrialization. The remaining hurdle was the mixture of silicone waste: could our method handle this ultimate challenge?

Waste elastomers, Industrial waste and waste Consumer Products. Silicone elastomers are more challenging substrates for depolymerization processes because they often exist in a complex formulated mixture comprised of fillers/additives, crosslinked silicone elastomers and catalysts. They are even more challenging at their end-of-life with lifespan pollution including many organic/inorganic contaminants, rendering their formulation even more complex. Polysiloxanes often account for 60-70% wt% while fillers (inorganics often based on silica or chemically modified SiO₂), pigments and catalyst often contribute in a range of 30-40 wt%. Considering the abundant of silicone elastomers in our society, several post-consumer silicone waste from our daily lives – such as nipple pads, cupcake molds, silicone sheets or water/liquid tubing were used as starting materials for the depolymerization process (*Fig. 3 and Table S4*). Interestingly, desired product **2** was obtained in high yields (90-99%, based on theoretical Si-O-containing moieties) (*Table S4*, entries 1-4). Then, industrial wastes, supplied by our industrial partner Elkem Silicone©, were also tested under optimized conditions (*Table S4*, entries 5-8). First, RTV1 and RTV2 formulated elastomers (room-temperature vulcanizates, with fillers) that are obtained through crosslinked using Tin (Sn) or Platinum (Pt) catalysts, were subjected to the depolymerization conditions. Interestingly, desired product **2** was obtained in an excellent yield (95%). Moreover, high-temperature vulcanization elastomer (HTV, with fillers) that was

crosslinked at elevated temperature in the presence of peroxide catalyst, was also evaluated. After 0.5 hour, chlorosilane **2** was again obtained in a quantitative yield. This protocol was extended to a more challenging HTV elastomer (formulation with additives and fillers densely crosslinked by peroxide and hydrosilylation at 170°C rather than ~120°C for classical HTV). Respectively 80% of **2** and 20% of **3** were recovered after depolymerization, even for this densely crosslinked silicone

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material. More interestingly, the chlorination of crosslinking knots was also detected in the crude mixture as the appearance of characteristic signals in ¹H-NMR spectra at 0.66 and 0.62 ppm (characteristic of Cl₂MeSi-CH₂CH₂-SiMeCl₂). Finally, a mixture of *all elastomers without sorting* (3 g) was subjected to these recycling conditions. After 2 hours, the crude mixture was distilled under reduced pressure (40°C, 200 mbar) to yield chlorosilane **2** and silyl ether **3** at 83% and 6%, respectively. A mixture of B₂O₃ and SiO₂ (2.2 g) and minimal silicone residues were also isolated after the distillation as a grey fine solid (see *Fig. S56 & S57*). This mixture could be used as base material in the production of borosilicate glass, boron nitride or boron carbide (25). These positive results demonstrate that this chemistry is highly selective and robust. No matter what fillers or catalyst residues are present in the silicone waste, the depolymerization of silicone backbones produces chlorosilane **2**, cornerstone of the silicone industry in almost quantitative yields based on D moieties. Chain-end functionalities could be recovered once again as valuable chain-capping agents for regeneration of catalogue oils for the Si industry.



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Fig. 3. Scope for the chemical recycling of silicone elastomers to corresponding chlorosilanes.

MECHANISM INVESTIGATION

To enhance our understanding and potentially tackle future challenges in silicon chemistry, the species resulting from the combination of chlorinated Lewis acids and GaCl₃ that allows the efficient formation of Si-Cl bonds from the Si-O bonds were examined using multi-nuclear NMR spectroscopy (*Fig. 4*). First, the mixture of BCl₃ & GaCl₃ (1:1 ratio) was analyzed in CD₂Cl₂ but the evidence of an anticipated Cl-bridged dimer was hard to detect (see ESI for detailed analysis, pp.S33-35). We beneficially added PPh₃ to the mixture in CD₂Cl₂ in a molar ratio of 1:1:2 (BCl₃/GaCl₃/PPh₃) and the *in situ* NMR analyses (¹¹B, ³¹P and ⁷¹Ga) were recorded at room

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temperature. The significant difference between the initial BCl_3 signal at 46.5 ppm and the new resonance at 3.91 ppm (d, $J = 154.6$ Hz for the $J^1\{^{11}\text{B}-^{31}\text{P}\}$ coupling) (**Fig. 4A**) was attributed to the signal of stabilized electrophile $[\text{BCl}_2(\text{PPh}_3)_2]^+$. This reveals the likely halide abstraction using 1 equiv. of GaCl_3 and 2 equiv. of PPh_3 , which agrees with tetracoordinate boronium species in solution (38). Moreover, the main resonance at -1.03 ppm (q, 154.6 Hz for the $J^1\{^{31}\text{P}-^{11}\text{B}\}$ coupling) was observed in the ^{31}P -NMR (**Fig. 4B**), indicating the interaction of triphenyl phosphine with BCl_2^+ . Additionally, one can identify the overlap of the characteristic quadruplet of $J^1\{^{31}\text{P}-^{11}\text{B}\}$ and minor septuplet of $J^1\{^{31}\text{P}-^{10}\text{B}\}$. The anionization of the gallium center was also confirmed by ^{71}Ga -NMR spectroscopy (**Fig. 4C**). The ^{71}Ga -NMR spectrum of active species exhibited a broad feature with two maxima at 250 and 270 ppm, consistent with analogous species $[\text{GaCl}_4]^-$ and $[\text{Ga}_x\text{Cl}_{3x+1}]^-$ to those identified for the P-donors (39,40). For the ^{71}Ga -NMR reference, $[\text{bmim}^+\text{GaCl}_4^-]$ was synthesized. Its main resonance was observed at ~250 ppm as a narrow signal, which corresponds to a nearly centrosymmetric tetracoordinate anion $[\text{GaCl}_4]^-$. Similar species can also be identified with AlCl_3 instead of GaCl_3 ; which comforted us in our assignment (centrosymmetric tetracoordinate anion $[\text{AlCl}_4]^-$ and polymeric analogues, see Fig. S53). In agreement with our spectroscopic study, we postulate a first cycle in the mechanism of the unusual electrophile depolymerization as below (**Fig. 4D**).

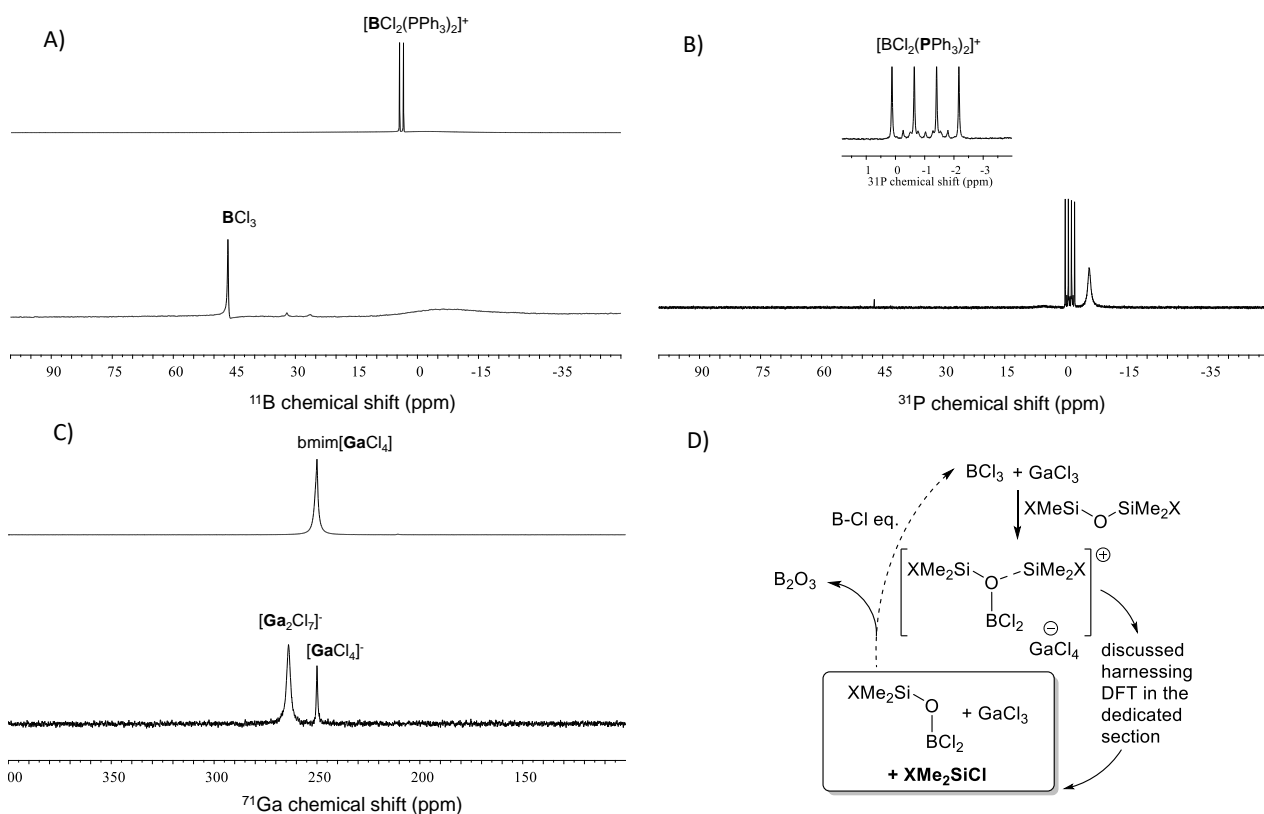


Figure 4. Multinuclear NMR spectrum of active species and postulated mechanism of depolymerization: Using triphenylphosphine to trap reactive $+\text{BCl}_2$ cation generated from 1:1 $\text{BCl}_3/\text{GaCl}_3$ mixture ($\text{PPh}_3/\text{BCl}_3/\text{GaCl}_3$ in a 2/1/1 ratio); a) ^{11}B -NMR, CD_2Cl_2 , 25°C ; b) ^{31}P -NMR, CD_2Cl_2 , 25°C ; c) ^{71}Ga -NMR, CD_2Cl_2 , 25°C ; d) postulated mechanism of the depolymerization reaction.

To raise our understanding of the key steps of the depolymerization mechanism, the “selective” cleavages of hexamethyl disiloxane (HMDS) and hexamethylcyclotrioxanes (D_3) have been investigated using various stoichiometric amounts of BCl_3 and/or $GaCl_3$ as chlorinating reagents in CD_2Cl_2 . HMDS and D_3 were selected to best represent the chain ends and main moieties (D) of the silicone waste to recycle, while retaining a manageable molecular dimension for the DFT calculation. The reactions were performed in 5-mm NMR tube under inert atmosphere and the corresponding multi-nuclear NMR analyses performed to detect some key intermediate species. BCl_3 can efficiently produce $TMSCl$ from HMDS (50% yield using 1 eq. BCl_3 with concomitant formation of $TMS-O-BCl_2$). Initially, boron trichloride was also able to cleave the D moieties of D_3 (Si-O-Si bond) to yield Si-Cl and Si-O-B bonds (see ESI, Figure S58-S61). Moreover, it favored the redistribution between mono-, di- and tri-alkoxy borate derivatives (**B1a**, **B2a**, **B3a**). However, it was not possible to cleave and chlorinate the corresponding O-Si-Cl bond to give Me_2SiCl_2 . In order to obtain the dimethyl dichlorosilane **2**, other metal chlorides such as $GaCl_3$ (Fe/ Al-based analogues can be utilized as well, see Table 1) must be involved in the catalytic cycle to break $Cl-(Me_2SiO)_x-BCl_2$ derivatives into Me_2SiCl_2 and correspond Cl-B-O derivatives that could further yield B_2O_3 with the help of catalysis (see dedicated section in ESI). Interestingly, $GaCl_3$ can also cleave HMDS to yield $\frac{1}{2}$ equiv. of $TMSCl$ and full conversion when using 2equiv. with respect to HMDS. However, $GaCl_3$ is unable to cleave D_3 . Only with the help of the mixture of HMDS/2equiv. $GaCl_3$ can we observe the formation of desired product **2**, albeit not quantitatively. These model reactions already suggest the need for a prerequisite complexation of a Lewis base to allow the formation of $[-LB-BCl_2^+GaCl_4^-]$ type species with Si-O-Si bond enacting as the *in situ* Lewis base.

As a first approach, we estimated the thermochemical driving force for these transformations by using tabulated bond dissociation energies. In particular, enthalpies of formation for Si-Cl/B-O formation and B-Cl/Si-O cleavage. (41-43). To our surprise, the tabulated values suggested an endothermic value of 17 kcal/mol (~ 72 kJ/mol), which is not what we would have expected for our system.

Performing calculations at the DFT level (see details in ESI section), we were able to rationalize and propose mechanisms that rationalize the reactivity of $GaCl_3$ and/or BCl_3 with D_3 (**Fig. 5**), thus unveiling the depolymerization mechanism. On first instance, the lack of reactivity of $GaCl_3$ alone is explained by the high Gibbs energy barrier required for the Si-O / Si-Cl bond metathesis (**TS1-Ga** ~ 31 kcal/mol) and its endergonicity (**Fig. 5a**). In the case of BCl_3 , boron oxophilicity weakens the Si-O bond enough to halve the activation energy of the Si-O / Si-Cl bond metathesis to 15 kcal/mol (**TS1-B**, **Fig. 5b**) and to thermodynamically favor Si-Cl and O- BCl_2 formations as detected by NMR. Of note, the following O-B-O cyclization *via* **TS2-B** is endergonic by *ca.* 6 kcal/mol and the subsequent chlorination / second Si-O cleavage (**TS3-B**) is kinetically prevented relative to the experimental conditions. The energetics of these two steps thus hinder the reaction to proceed further, in line with experimental results. For both Lewis acids, when used independently, Si-O / Si-Cl bond metathesis transition states **TS1-Ga** and **TS1-B** feature distorted square-pyramidal geometries at Si (**Fig. 5c**), a pattern that differs when both $GaCl_3$ and BCl_3 are combined (*vide infra*).

In addition, we calculated bond dissociation energies (BDE) on an opened D_3 molecule by BCl_3 (see ESI, **Table S5** and **Figure S62**) and we obtained an exothermic value of -15 kcal/mol for the transformation of B-Cl/Si-O to B-O/Si-Cl bonds. A very different value from the ΔH calculated from tabulated ones and in better agreement with the experimental results.

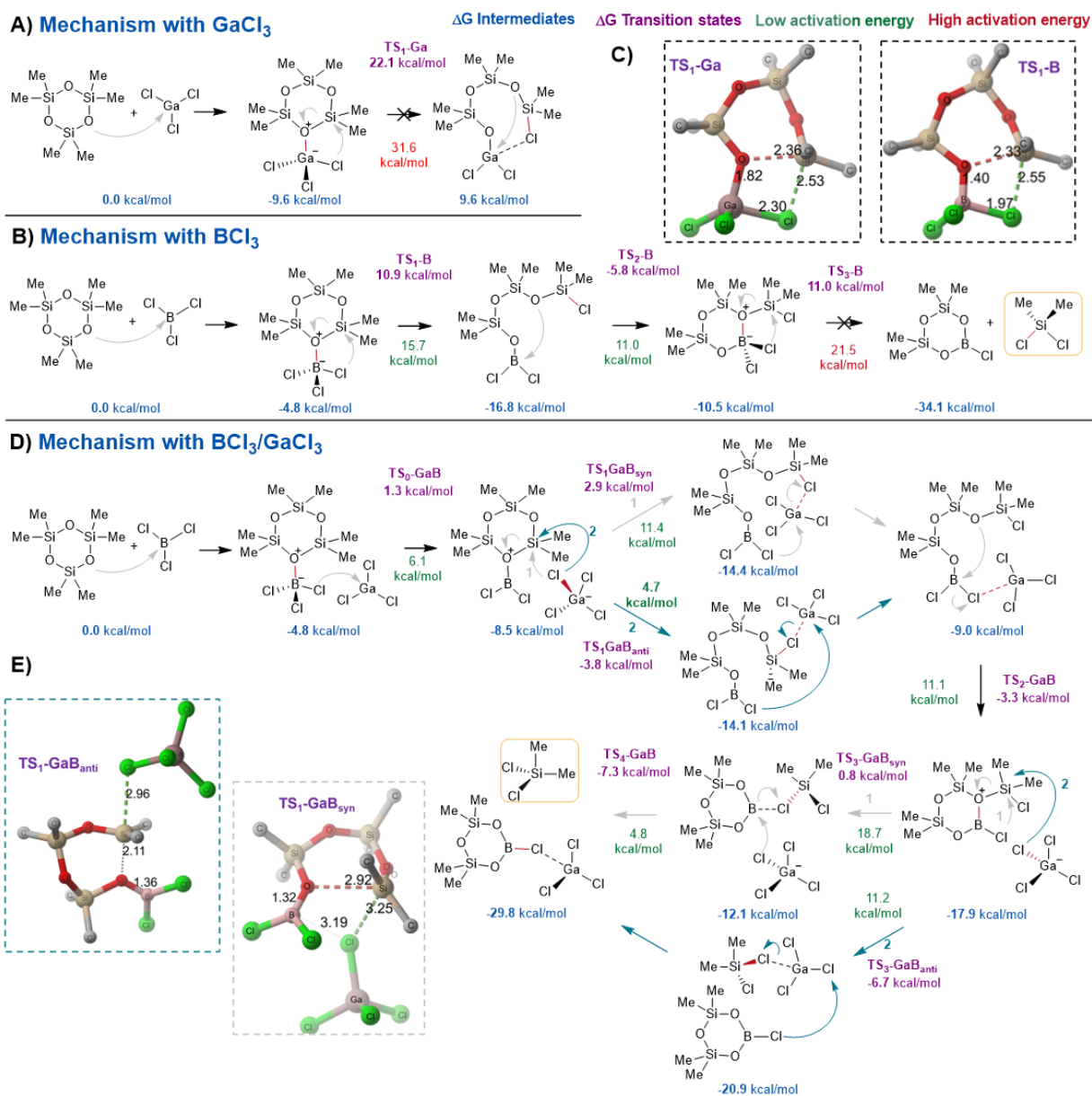


Figure 5. Mechanistic proposals for the formation of Me₂SiCl₂ from D₃: in presence of GaCl₃ (A), BCl₃ (B) or both GaCl₃ and BCl₃ (D), supported by calculations at the DFT level of theory. The transition state structures of four possible Si-O cleavage/ Cl-Si formation (C, T₁-Ga and T₁-B; E, T₁-GaB anti and syn) are depicted.

When D₃ reacts with both BCl₃ and GaCl₃, the formation of GaCl₄⁻ by Cl transfer from B to Cl upon O-B bond formation is virtually barrierless and thermodynamically favored (~ 2 kcal/mol *via* TS₀-GaB) with a gain of ~ 4 kcal/mol over the Lewis-adduct. This exchange reaction is driven by boron's preference to form B-O over B-Cl bonds, weakening consequently the (B)O-Si bond and raising the cationic character of the vicinal silicon atoms (32). This boron to gallium Cl transfer reaction also impacts the geometry at Si that evolves from tetrahedral to distorted trigonal pyramid.

From this geometry, the Si can undergo an O to Cl exchange mediated by an attack of GaCl_4^- at both Si apical positions of a transient and hypervalent trigonal bipyramid (**TS1-GaB_{syn}** and **TS1-GaB_{anti}**, *Fig. 5d & 5e*). The Gibbs energy barrier for the O to Cl exchange is lowered by 6 kcal/mol when Cl and O are *trans* to each other. In contrast to the BCl_3 case, the formation of new B-O bonds continues (**TS2-GaB**) at expenses of Cl release by B and transiently captured by GaCl_3 , which weakens again the adjacent O-Si bonds to yield Me_2SiCl_2 (**TS3-GaB_{anti}**). Lowering this barrier almost 10 kcal/mol, in comparison to BCl_3 .

CONCLUSION

We present a universal chemical depolymerization for all silicone waste, including elastomers with fillers, which represent a substantial fraction (>40%) of post-consumer waste. This strategy advantageously uses the thermodynamic lever of B-Cl / B-O bonds exchange that offsets the supposedly unfavorable Si-O/B-Cl to Si-Cl/B-O conversion by -15 kcal/mol. The side-product of recycling is thus boron oxide B_2O_3 , a raw material oxide for borosilicate glass. Ga catalysis favors the transformation by lowering the activation energy ~10 kcal/mol, which corresponds to a ~ 36-million-fold (3.6×10^7) kinetic enhancement. The recovered (methyl)chlorosilanes, key industrial intermediates known as MCS in the silicon industry, are then recovered by straightforward distillation. Our method sidesteps the energy-intensive metallurgy and Müller-Rochow process, lowering significantly the carbon footprint of silicone materials when compared to starting anew from native quartz. NMR spectroscopy (observed nuclei: ^{11}B , ^{29}Si , ^{71}Ga and ^{31}P to spy the intermediates) analyses allowed us to pinpoint very favorable Ga-catalyzed intermediates (such as $[-\text{LB}-\text{BCl}_2^+\text{GaCl}_4^-]$, with LB being a Si-O-Si moiety) and propose a mechanism for the transformation as unveiled by modeling at the DFT level. This work paves the road for the circular economy of silicon.

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- 15 36. A mixture of oligomers of Cl(Ph₂SiO)_xSiPh₂Cl, likely including Ph₂SiCl₂, for the recycling of copolymer 14 was found, indicated by the appearance of NMR resonances at 7.76 and 7.36 ppm in ¹H NMR analysis, as evidenced by Figure S32. It is likely that recovering the Ph₂SiCl₂ quantitatively would necessitate harsher reactive distillation conditions.
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Conceptualization: JR, VM

Methodology: NDV, VM, JR

Resources: ABM, ND, MB, RL

NMR characterization: DG, AB

DFT calculation: SRG, MEP

Visualization: NDV, VM, JR

Project administration, Supervision: JR, VM, JM

Writing – original draft, review & editing: NDV, VM, JR with participation of all authors

Competing interests: N.D.V, A. B.-M., N.D., J. R. and V.M are also the inventors of a patent application WO2023222749A1, released on 23rd November 2023.

Data and materials availability: All data, code, and materials used in the analysis must be available in some form to any researcher for purposes of reproducing or extending the analysis. Include a note explaining any restrictions on materials, such as materials transfer agreements (MTAs). Note accession numbers to any data relating to the paper and deposited in a public database; include a brief description of the data set or model with the number. If all data are in the paper and supplementary materials, include the sentence “All data are available in the main text or the supplementary materials.”