

# Carbon-Supported Potassium Hydride for Efficient Low-Temperature Desulfurization

Fei Chang<sup>[a]</sup> and Alexey Fedorov\*<sup>[a]</sup>

In memory of Robert H. Grubbs

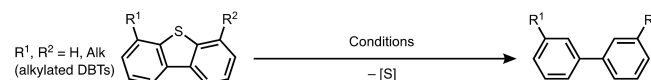
**Abstract:** The industrial removal of organosulfur impurities from fossil fuels relies on transition-metal-based catalysts in harsh conditions (ca. 400 °C, up to 100 bar H<sub>2</sub>), yet desulfurization (DS) of refractory alkyl dibenzothiophenes (DBTs) remains challenging. Here, we report that carbon-supported potassium hydride (KH/C) enables efficient DS of DBTs in mild conditions, viz. >97% conversion of DBTs is achieved at 165 °C in 3–6 h while the yields of respective biphenyls are 84–95% by using only 15% excess of KH per a C–S bond. In

addition, KH/C allows to lower the concentration of 4,6-Me<sub>2</sub>DBT in the mesitylene solution from 1000 ppm to < 3 ppm (165 °C, 20 h) and provides deoxygenation, denitrogenation and catalytic aromatic hydrogenation reactions. DS of various sulfur heterocycles by using KH/C, a transition-metal-free material based on earth abundant elements, is viable at low temperature and has prospects for the further development towards decentralized removal of organosulfur species from fossil fuels.

## Introduction

The removal of organosulfur impurities from petroleum products in general and transportation fuels in particular is essential for the downstream catalytic processes and environmental protection.<sup>[1–2]</sup> Hydrodesulfurization (HDS), an industrial process for the removal of organosulfur compounds from fossil fuels, relies on heterogeneous catalysts such as MoS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> promoted with cobalt or nickel. Those catalysts are typically utilized at ca. 400 °C under H<sub>2</sub> pressures of up to 100 bar.<sup>[3–4]</sup> Even under these forcing conditions, the removal of alkylated dibenzothiophenes (DBTs), such as 4,6-Me<sub>2</sub>DBT or 4,6-Et<sub>2</sub>DBT by HDS is challenging (Scheme 1).<sup>[5–9]</sup> Because HDS is energy intensive, there is an interest in alternative routes that are more environmentally friendly and also potentially amenable to decentralized desulfurization (DS).<sup>[10]</sup>

Several strategies for the reductive DS under mild conditions (i.e., at low temperatures) have been developed. One early approach relies on excess of Raney-Ni.<sup>[11]</sup> Alternatively, stoichiometric amounts of alkyl Grignard reagents or, more recently, an organosilane (such as EtMe<sub>2</sub>SiH) in a combination



• Currently used centralized industrial HDS: Co(Ni)MoS<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> at ca. 400 °C and ca. 100 bar H<sub>2</sub>

• Approaches towards decentralized deep desulfurization

• (Et<sub>3</sub>SiH + KO<sup>t</sup>-Bu) at ca. 165 °C (KOSi method). Efficient but leaves residual K and Si in solution

• This work: DS using KH/C at 50 °C – 165 °C. Efficient, avoids the use of Et<sub>3</sub>SiH, no leaching of K

**Scheme 1.** Methods for desulfurization of recalcitrant sulfur heterocycles.

with a Ni-based catalyst have been applied for the DS of aryl methyl thioethers.<sup>[12–13]</sup> In addition, Ni, Co and Fe-based catalysts supported by the phosphoramidate (R<sub>3</sub>P=N<sup>-</sup>) ligands have been shown to catalyze desulfurization when used in combination with NaH or KH, typically at 110–140 °C.<sup>[14]</sup> Alkali metals (Li, Na, K) have been used in DS reactions as well,<sup>[15–17]</sup> including DS of petroleum residues and coal.<sup>[18–19]</sup> While alkali metals are effective for the DS of alkylated dibenzothiophenes, which yields biaryls and alkali metal sulfides (Scheme S1),<sup>[20]</sup> an excess of an alkali metal is often required (usually, 10-fold and higher), which is not atom economical and generates waste. In addition, the reaction typically involves an aqueous workup when Li and Na are used (see Table S1 and references therein).

A mixture of potassium *tert*-butoxide and triethylsilane (1 : 1 ratio, the so-called Grubbs-Stoltz reagent) has been reported to efficiently desulfurize a range of refractory organic sulfur substrates (Scheme 1).<sup>[21]</sup> Those batch DS reactions have been typically conducted at 165 °C for 40 h and utilized three equivalents of the KO<sup>t</sup>-Bu/Et<sub>3</sub>SiH reagent per one mol of a substrate. Interestingly, the Grubbs-Stoltz reagent showed a high DS efficiency with alkylated dibenzothiophenes, similar to that displayed by the alkali metals.<sup>[21]</sup> For instance, the KO<sup>t</sup>-Bu/Et<sub>3</sub>SiH reagent allows to lower the content of 4,6-Me<sub>2</sub>DBT in the spiked diesel from ca. 10000 ppm to 2.4 ppm, although in this

[a] Dr. F. Chang, Dr. A. Fedorov  
Laboratory of Energy Science and Engineering  
Department of Mechanical and Process Engineering  
ETH Zürich  
8092 Zürich (Switzerland)  
E-mail: fedoroal@ethz.ch

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case a 0.5 M concentration (i.e., a large excess) of KOt-Bu and Et<sub>3</sub>SiH has been used. The application of KOt-Bu with Et<sub>3</sub>SiH for DS provides, at least initially, a homogeneous reaction mixture and thereby leads to a high concentration of K and Si species in solution after the DS reaction. Contamination of the sulfur-lean fuel by such species, and the high price of the used reagents, limit the practical advantageous of this method for the DS of fuels.

It has been recently suggested that KOt-Bu/Et<sub>3</sub>SiH generates potassium hydride at ca. 130 °C.<sup>[22]</sup> This result implies that KH may play an important role in the DS activity of the Grubbs-Stoltz reagent.<sup>[21]</sup> In general, the DS activity of KH remains underexplored. To the best of our knowledge, it has only been reported that heating DBT with 2.5 equiv. of KH in THF (110 °C, 16 h) leads to 2-phenylthiophenol in 78 % yield and biphenyl in 10 % yield at >99 % conversion of DBT.<sup>[23]</sup> Performing this reaction under 34 bar of H<sub>2</sub> and at otherwise identical conditions lowers conversion of DBT to 93 % and yields 2-phenylthiophenol and biphenyl in 81 % and 1 %, respectively.<sup>[23]</sup>

Here, we report that a transition-metal-free carbon-supported potassium hydride (KH/C) enables reductive desulfurization of C–S bonds in a variety of organosulfur substrates under mild conditions (starting from ca. 50 °C), including refractory DBTs. Yields of desulfurized hydrocarbons obtained using KH/C in mesitylene, toluene or cyclohexane often exceed 90 %, achieved with only ca. 15 % molar excess of KH per a C–S bond, and without leaching of K into solution. In mesitylene, KH/C enables a chemoselective DS of 4,6-Me<sub>2</sub>DBT in the presence of di-*n*-octyl sulfide. When conducted under 10 bar of H<sub>2</sub>, KH/C catalyzes the hydrogenation of an unsubstituted phenyl ring in biphenyl derivatives to form a cyclohexyl group. In addition, the potential of KH/C for the removal of other heteroatoms is demonstrated using dibenzofuran and 9-phenylcarbazole as model substrates that undergo deoxygenation and denitrogenation reactions, respectively. Similarly to the results obtained with the Grubbs-Stoltz reagent,<sup>[24]</sup> the incorporation of deuterium into the desulfurized products takes place when KH/C is applied in toluene-d<sub>8</sub>, in agreement with similar reaction pathways for both reagents.

## Results

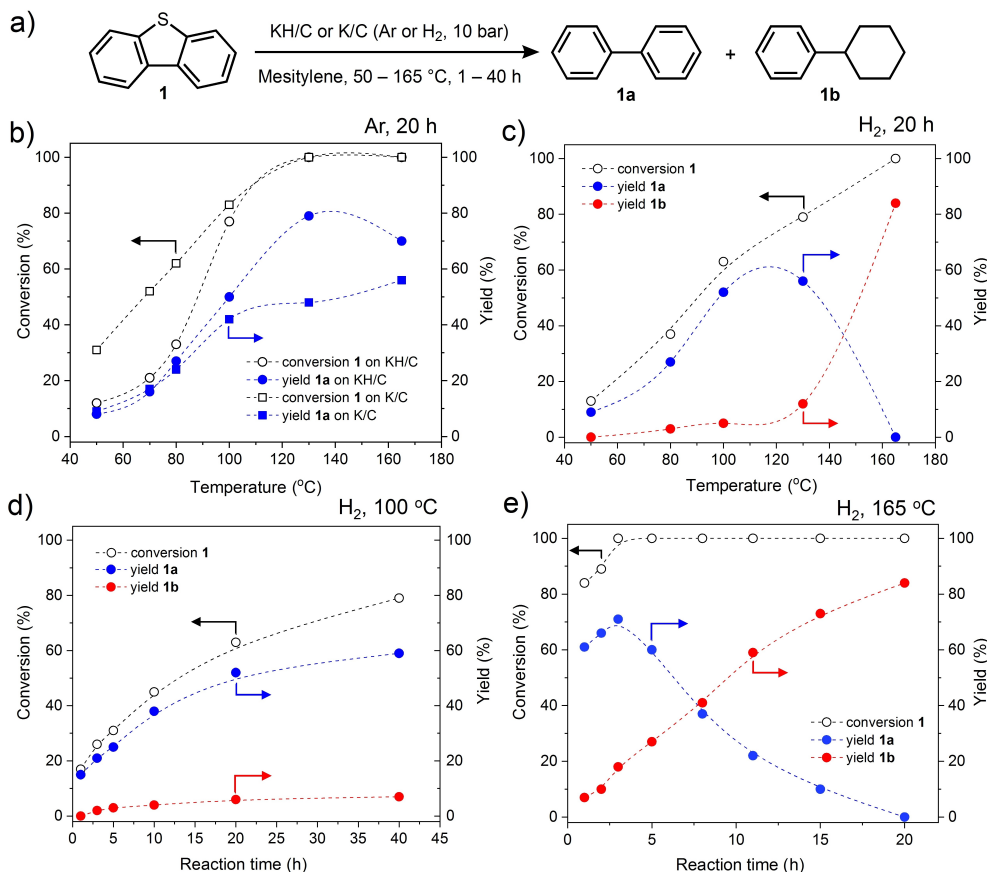
KH/C was prepared by heating at 110 °C metallic potassium mixed with a carbon support (graphite, surface area ca. 500 m<sup>2</sup> g<sup>-1</sup>) under 10 bar of H<sub>2</sub> for 10 h, following a known melt infiltration method (see Supporting Information for details).<sup>[25]</sup> The loading of K in KH/C is 30.1 wt% according to the inductively coupled plasma optical emission spectroscopy (ICP-OES), which is close to the nominal loading of 30 wt% (Table S2). The content of various transition metals in KH/C is below the detection limit of the ICP-OES (<1 ppm, Table S2). X-ray diffraction (XRD) pattern of KH/C contains peaks attributed to graphite (at 26°, 43° and 54°) and to potassium hydride (at 27°, 31°, 45°, 53° and 56°, Figure S1), consistent with the oxidation of metallic K by H<sub>2</sub>. The crystallite size of KH in KH/C estimated by the Scherrer equation is ca. 40 nm. Temperature-

programmed desorption (TPD) was performed to quantify the amount of KH in KH/C. Three peaks corresponding to the release of H<sub>2</sub> are observed, i.e., at ca. 171, 327 and 400 °C (Figure S2). The quantity of H<sub>2</sub> released from KH/C during the TPD experiment under an Ar flow is ca. 4.5 mmol H<sub>2</sub> g<sub>KH/C</sub><sup>-1</sup>, which is higher than the quantity of H<sub>2</sub> expected from the KH loading by ICP-OES (ca. 3.8 mmol H<sub>2</sub> g<sub>KH/C</sub><sup>-1</sup>). This result suggests that KH/C contains additional chemisorbed H<sub>2</sub>. A reference K/C material was prepared as described above for KH/C except that an Ar atmosphere was used in place of H<sub>2</sub>. The K/C material has a K loading of 28.9 wt%, according to ICP-OES, and is amorphous by XRD (Figure S1).

Dibenzothiophene (**1**) was used to evaluate the DS reaction conditions using KH/C and compare results to K/C and commercial KH. Towards this end, a 0.03 M solution of **1** in mesitylene was stirred for 20 h under Ar with 1.15 equiv. of KH (in KH/C and commercial KH) or K (in K/C) per C–S bond of **1** while the temperature was varied from 50 to 165 °C (Figure 1a). Unless specified otherwise, an internal standard (tridecane) was added after the reaction, the reaction mixture filtered and conversion of **1** and yields of the formed products quantified by gas chromatography-mass spectrometry (GC-MS) without any additional workup. DS of **1** provides biphenyl (**1a**) as the only product already at 50 °C, obtained in 8 % yield at 11 % conversion of **1** (Figure 1b). At 130 °C, conversion of **1** is full and **1a** is obtained in 79 % yield. At 165 °C, yield of **1a** is 70 % and no other product is detected by GC. In contrast, a control experiment with commercial KH performed at 165 °C gives only 26 % conversion of **1** and 17 % yield of **1a** (Table S3).

The lower yield of **1a** with KH/C at 165 °C relative to 130 °C is likely due to the increased reactive adsorption of **1** (or intermediates from **1** to **1a**) onto the KH/C material, possibly owing to a partial decomposition of KH to K and H<sub>2</sub> on KH/C at the higher reaction temperature used. Indeed, control experiments indicate that the reactive adsorption of **1** is stronger on K/C compared to KH/C since, for instance, below 80 °C, conversion of **1** on K/C is about two times higher than that on KH/C (62 % and 32 %) yet the yields of **1a** are comparable (25 % and 27 %, Figure 1b). A similar trend is also observed at 130 °C and 165 °C, that is, K/C shows a complete conversion of **1** but lower yields of **1a** compared to KH/C, likely owing to a higher amount of strongly adsorbed species formed due to the reactive adsorption of **1** on K/C (Figure 1b). Noteworthy, an Ar-TPD experiment performed using the dried material obtained after stirring KH/C in mesitylene at 165 °C for 20 h shows the lack of detected H<sub>2</sub>; in addition, the diffraction peaks due to the KH phase in KH/C are no longer observed in the recovered material (Figures S1 and S2).<sup>[26]</sup> These results are consistent with the decomposition of KH/C to K/C in the conditions mentioned above.

Aiming to stabilize KH/C, we performed the DS experiments under H<sub>2</sub> pressure. Products **1a** and phenylcyclohexane (**1b**) form when DS of **1** is performed under a H<sub>2</sub> atmosphere (Figures 1a,c). With the increase of the reaction temperature from 50 °C to 130 °C, the yield of **1b** gradually rises from 0 % to 12 % before raising sharply to 84 % at 165 °C. The yield of **1a** increases from 9 % at 50 °C to 54 % at 130 °C and then it



**Figure 1.** a) Desulfurization of **1** using KH/C or K/C at 50 °C–165 °C in b) Ar (10 bar) and c) DS of **1** using KH/C in H<sub>2</sub> (10 bar). DS of **1** using KH/C under 10 bar of H<sub>2</sub> during 1 h–40 h at d) 100 °C and e) 165 °C. The molar ratio of K (in KH/C or K/C) to **1** was 2.3:1. The lines are added to guide the eye. K<sub>2</sub>S/C forms along with **1a** and **1b**.

decreases to 0% at 165 °C, explained by the hydrogenation of **1a** to **1b**. The desulfurization of **1** using KH/C was then compared at 100 °C and 165 °C under 10 bar of H<sub>2</sub>. After 40 h at 100 °C, **1a** and **1b** form in 59% and 7% yields, respectively, at 79% conversion of DBT (Figure 1d). The low yield of **1b** indicates that the hydrogenation reaction is slow at 100 °C. In contrast, conversion of **1** reaches 82% after 1 h at 165 °C, and yields of **1a** and **1b** are 61% and 8%, respectively (Figure 1e). Conversion of **1** is full after 3 h at 165 °C and at this time yields of **1a** and **1b** are 71% and 19%, respectively. Longer reaction times lead to the consumption of **1a** by its hydrogenation to **1b**, that is, no **1a** is detected after 20 h of reaction whereas the yield of **1b** is 84%. In contrast, commercial KH gives only 10% conversion of **1** and 7% yield of **1b** in these conditions (165 °C, 20 h, see Table S3). If a lower hydrogen pressure is used, i.e. 2 bar or 5 bar, the yield of **1b** on KH/C after 20 h at 165 °C is also lower, i.e. 7% or 38%, respectively, while **1a** is the major product, formed in 80% or 42% yield, respectively, at the complete conversion of **1** (Table S4). These results suggest that phenylcyclohexane is a secondary reaction product formed via hydrogenation of biphenyl. We note that the hydrogenation activity of K and KH with unsaturated hydrocarbons has been reported,<sup>[27–28]</sup> including also hydrogenation of biphenyl to

phenylcyclohexane, and the mechanistic pathways have been discussed.<sup>[26]</sup>

By using **1a** as the substrate (165 °C, 10 bar H<sub>2</sub>, 20 h), the hydrogenation of **1a** to **1b** is catalytic on KH/C with the turnover numbers, TON, up to at least 23 (TON is calculated as mol of the newly formed C–H bond per mol of KH used, Table S5). We observe that **1b** is the only hydrogenation product in these conditions. A control experiment shows that no **1b** forms on a bare carbon support (Table S5). With the absence of H<sub>2</sub> and using the typical 2.3:1 molar ratio of KH/C to **1a**, only 3% yield of **1b** is obtained (Table S5, entry 6). The subsequent hydrogenation of **1b** to bicyclohexane (**1c**) can proceed at a higher pressure of 100 bar of H<sub>2</sub>, yet the yield of **1c** is only 3%, likely because of the steric effect of the cyclohexyl group in **1b** (Table S6).

XRD profile of the used KH/C material collected after the DS reaction of **1** (165 °C, 20 h, 10 bar H<sub>2</sub>) shows discernable peaks attributed to K<sub>2</sub>S on C (Figure S3). HADDF-STEM images and EDX mappings reveal the high dispersion of K and S on the KH/C after the desulfurization reaction (165 °C, 20 h, 10 bar Ar); a similar distribution of K and S is observed on the used K/C (Figure S4).

Decreasing by two fold amount of the used KH per mol of **1**, i.e. from ca. 2.3:1 to 1.15:1, lowers the conversion of **1** from

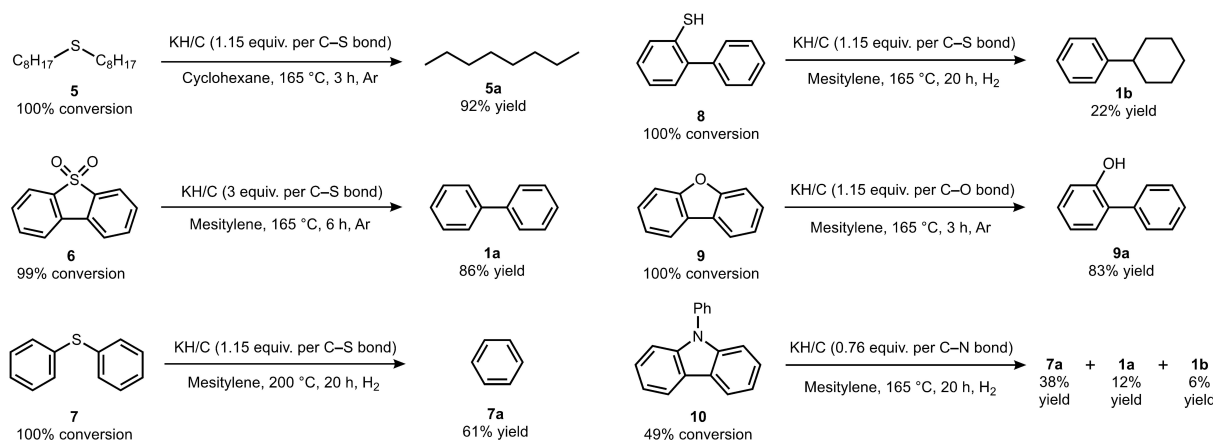
complete to 46% (165 °C, 20 h, 10 bar H<sub>2</sub>, see Table S7). In addition, the distribution of products changes notably, i.e. from 84% of **1b** (the sole detected product) when the 2.3:1 ratio is used, to only 5% of **1b** and 40% of **1a** with the 1.15:1 ratio of KH/C:DBT. This is explained by the conversion of a large part of KH/C to K<sub>2</sub>S/C when the 1.15:1 molar ratio of KH/C:DBT is used, and the inactivity of K<sub>2</sub>S/C in the hydrogenation of **1a** to **1b**. Attempting DS of **1** using KH/C that had been recovered and treated under 100 bar of H<sub>2</sub> at 200 °C for 20 h, gives only 1% conversion of **1** (Table S8). This result is consistent with the unfavorable thermodynamics for the regeneration of K from K<sub>2</sub>S via the thermal treatment in H<sub>2</sub> at the relatively low temperatures used in this work (Figure S5).

Refractory alkylated DBTs also succumbed to the desulfurization by KH/C. The DS of monomethyl, dimethyl and diethyl substrates **2–4** proceeds smoothly and gives biaryls **2a–4a** in 91–95% after 6 h at 165 °C under Ar (Table 1, entries 1–3). High yields (82–90%) of biaryls **2a–4a** are still obtained when decreasing the reaction temperature to 130 °C (Table S9). When Ar atmosphere is replaced by H<sub>2</sub>, the hydrogenation of the unsubstituted phenyl ring occurs with the formation of **2b** in 23% yield (Table 1, entry 4). Noteworthy, **3b** and **4b** are not observed, highlighting that the alkyl-substituted phenyl rings are not hydrogenated using KH/C in those conditions (Table 1, entries 5 and 6).

KH/C desulfurizes aliphatic di-*n*-octyl sulfide (**5**) to *n*-octane (92% yield) at the full conversion of **5** when the reaction is performed in cyclohexane at 165 °C for 3 h under Ar (Scheme 2). Note that dialkylsulfides, including **5**, are generally challenging substrates for the DS with sodium, i.e. no desulfurization took place when (*n*-C<sub>6</sub>H<sub>13</sub>)<sub>2</sub>S, (*n*-C<sub>8</sub>H<sub>17</sub>)<sub>2</sub>S or (*n*-C<sub>12</sub>H<sub>25</sub>)<sub>2</sub>S have been heated with Na at 110 °C or at 164 °C; however, increasing the temperature to 254 °C in tetradecane solvent has been reported to provide the corresponding alkanes in high yields, along with small amounts of the corresponding alkylthiols.<sup>[29]</sup> Interestingly, we observe no conversion of **5** in mesitylene at 165 °C (Table S10). This may be due to the prevailing competitive adsorption of mesitylene relative to di-*n*-octyl sulfide on the active sites of KH/C, given the notably higher concentration of mesitylene than di-*n*-octyl sulfide in the reaction mixture. Interestingly, a chemoselective DS of **3** occurs when an equimolar mixture of **3** and **5** is treated with KH/C in mesitylene, however, when this reaction is conducted in cyclohexane, both **3** and **5** undergo desulfurization (Table S11). Dibenzothiophene sulfone (**6**) provides **1a** in 86% yield at 99% conversion of **6** when using KH/C (165 °C, 6 h, Ar, see Scheme 2). The desulfurization of diphenyl sulfide (**7**) in mesitylene requires a higher temperature of 200 °C to reach full conversion (20 h, H<sub>2</sub>) and gives benzene (**7a**) in 61% yield (Scheme 2). The yield of **7a** decreases to 40% and to 18%

**Table 1.** Desulfurization of alkylated dibenzothiophenes using KH/C under 10 bar of Ar (entries 1–3) or H<sub>2</sub> (entries 4–6).

Entry	Substrate	Gas phase at 10 bar	Reaction time [h]	Conversion of <b>2–4</b> [%]	Yield of <b>2a–4a</b> [%]	Yield of <b>2b–4b</b> [%]
1	R <sup>1</sup> = Me, R <sup>2</sup> = H (4-MeDBT, <b>2</b> )	Ar	6	100	91	0
2	R <sup>1</sup> = R <sup>2</sup> = Me (4,6-Me <sub>2</sub> DBT, <b>3</b> )	Ar	6	97	92	0
3	R <sup>1</sup> = R <sup>2</sup> = Et (4,6-Et <sub>2</sub> DBT, <b>4</b> )	Ar	6	98	95	0
4	<b>2</b>	H <sub>2</sub>	20	100	66	23
5	<b>3</b>	H <sub>2</sub>	20	100	94	0
6	<b>4</b>	H <sub>2</sub>	20	100	97	0



**Scheme 2.** Substrate scope of the reductive desulfurization, deoxygenation and denitrogenation reactions using KH/C under Ar or H<sub>2</sub>. Conversion of **6** was quantified by <sup>1</sup>H NMR. After the reaction with **9**, isopropanol was added to the reaction mixture and stirred for 3 h at room temperature prior to the product analysis by GC-MS.

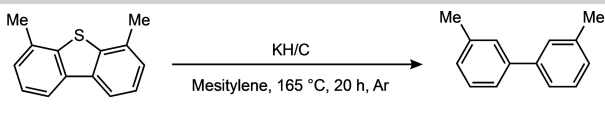
when the reaction is performed at 165 °C and 130 °C, respectively (Table S12). Interestingly, both the conversion of **7** and the yield of **7a** are consistently lower when Ar is used in place of H<sub>2</sub>, disregard of the reaction temperature (130, 165 or 200 °C, Table S12). DS of 2-phenyl-thiophenol (**8**) on KH/C at 165 °C under H<sub>2</sub> also leads to a complete conversion, however, **1b** is obtained only in 22% yield, likely due to the strong adsorption of the reaction intermediates on KH/C.<sup>[30–31]</sup> The treatment of the reaction mixture with isopropanol does not improve the yield of **1b** (Table S13). These results suggest that potassium 2-phenylthiophenoxide is an unlikely intermediate in the DS of **1**.

In addition, KH/C can be used for the reductive cleavage of C–O and C–N bonds. The treatment of dibenzofuran (**9**) with KH/C at 165 °C for 3 h gives 100% and 76% conversion of **9** under Ar and H<sub>2</sub>, respectively (Table S14, entries 1–2). That being said, only 1% yield of 2-phenylphenol (**9a**) is detected in the supernatant after the reaction. However, stirring the reaction mixture with isopropanol allows to quantify 83% of **9a** when the reaction is performed under Ar (Scheme 2), or 36% of **9a** when under H<sub>2</sub>. This suggests a strong adsorption of potassium 2-phenylphenoxide (gives **9a** upon protonation by isopropanol) on the reacted KH/C. When the reaction is performed under H<sub>2</sub> for 8 h, 2-cyclohexylphenol and **1b** form in 8% and 4% yields, respectively (Table S14). Denitrogenation of 9-phenylcarbazole (**10**) in mesitylene at 165 °C under Ar provides benzene in 35% yield as the only detected product, at 35% conversion of **10** (Table S15). However, performing this reaction under H<sub>2</sub> increases conversion of **10** to 49% and gives **7a**, **1a** and **1b** in 38%, 12% and 6% yields, respectively (Scheme 2). Increasing the ratio of KH/C to **10** from 2.3:1 to 3.3:1 does not increase the yield of these products (Table S15). However, increasing the H<sub>2</sub> pressure from 10 to 100 bar leads to a higher conversion of **10**, i.e. it increases from 49% to 80%, and gives **7a** and **1b** in 51% and 18% yields, respectively (Table S15, entry 5). An additional workup of the reaction mixture of **10** using isopropanol does not lead to higher yields of these products (Table S15).

Furthermore, KH/C allows to reduce the sulfur content of 4,6-Me<sub>2</sub>DBT (**3**) to low ppm levels, that is, concentration of [S] due to **3** in mesitylene solution can be lowered from 1000–100 ppm to [S] < 3 ppm, i.e., ultra-deep DS,<sup>[32–33]</sup> by treating these solutions with 3 molar equivalents of KH/C at 165 °C for 20 h (Table 2, entries 1–2). With 10 ppm of **3** in the solution, a similar low [S] content (2.4 ppm) is achieved with 12 equivalent of KH/C (Table 2, entry 3).

Lastly, DS of **1** was performed using KH/C and K/C in toluene-d<sub>8</sub> to probe the H/D exchange with the solvent under Ar atmosphere. At ca. 2–6% conversion of **1** and ca. 1% yield of **1a**, no deuterium incorporation into **1a** is observed using either KH/C or K/C as the distribution of the mass-to-charge ratios of **1a** obtained in toluene-d<sub>8</sub> does not differ from that in non-deuterated mesitylene (Figure S6). However, when conversion of **1** reaches 10–33% (20 h at 50 °C), a partial incorporation of deuterium into **1a** is observed with both KH/C and K/C, seen by the appearance of peaks with m/z higher than 154, i.e., up to m/z=159 for K/C and m/z=164 for KH/C (Figure S6). An intense peak at m/z=164, i.e., of the fully deuterated **1a**, is

**Table 2.** Ultra-deep desulfurization of 4,6-Me<sub>2</sub>DBT by using KH/C.<sup>[a]</sup>



Entry	Molar ratio KH/C:3	[S] initial [ppm]	[S] after DS [ppm]
1	3	1000	2.6
2	3	100	2.7
3	12	10	2.4

[a] Concentrations of [K] in the initial mesitylene solution of **3** and in the reaction mixture after the DS tests are lower than the instrumental ICP-OES limit of detection (< 1 ppm).

observed on KH/C at the full conversion of **1**, which gives 74% yield of **1a** after 20 h at 165 °C (Figure S6). In these conditions, K/C gives 52% yield of **1a** with a broad distribution of m/z ratios, up to m/z=164. These results indicate that the incorporation of deuterium into **1a** is faster on KH/C than on K/C. Control experiments show that the H/D exchange between biphenyl and toluene-d<sub>8</sub> leads to the fully deuterated **1a** (m/z=164) and **1b** (m/z=176) when heating **1a** with KH/C in toluene-d<sub>8</sub> (165 °C, 20 h, Figure S7). The H/D exchange proceeds similarly when using benzene-d<sub>6</sub> as the solvent instead of toluene-d<sub>8</sub> (Figure S7). No deuteration of **1** was observed in any of the reaction mixtures discussed above. When deoxygenation of **9** performed in toluene-d<sub>8</sub> at 165 °C in Ar for 3 h, the deuterium incorporation into **9a** is also observed, giving m/z of **9a** distributed from 170 to 180 (Figure S8). Note that KH has been reported to catalyze the H/D exchange, i.e., the exchange between D<sub>2</sub> and toluene (or H<sub>2</sub> and toluene-d<sub>8</sub>) under reflux and 5 bar H<sub>2</sub>(D<sub>2</sub>).<sup>[34]</sup>

## Conclusion

We have reported that KH/C is an efficient reagent for the reductive cleavage of C–S bonds in a variety of sulfur-containing compounds, including ultra-deep desulfurization. The DS performance of KH/C is comparable to that of the KOt-Bu/Et<sub>3</sub>SiH reagent, and their H/D exchange reactivity with deuterated solvents is also similar. While KH/C provides complete desulfurization, for instance of DBT to biphenyl, only a partial desulfurization of DBT to 2-phenyl-thiophenol has been reported previously using unsupported KH in THF,<sup>[23]</sup> both conversion of DBT and yield of biphenyl are notably lower when commercial KH is used in place of KH/C under otherwise identical conditions. No leaching of K from KH/C to the reaction mixture is observed. These results highlight benefits of using KH dispersed on graphite for the DS applications. Future work shall focus on the electrocatalytic regeneration of the used KH/C material (i.e., the transformation of K<sub>2</sub>S/C to K/C),<sup>[20]</sup> and on the elucidation of the underlying mechanism of DS on KH/C, which likely involves single electron transfer steps (Scheme S2).<sup>[35]</sup>

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## Conflict of Interest

A patent application based on the findings of this work has been submitted.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** alkyl dibenzothiophenes · desulfurization · hydrides · potassium · radical ions

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