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Adsorptive on-board desulfurization over multiple cycles for fuel-cell-based auxiliary power units operated by different types of fuels

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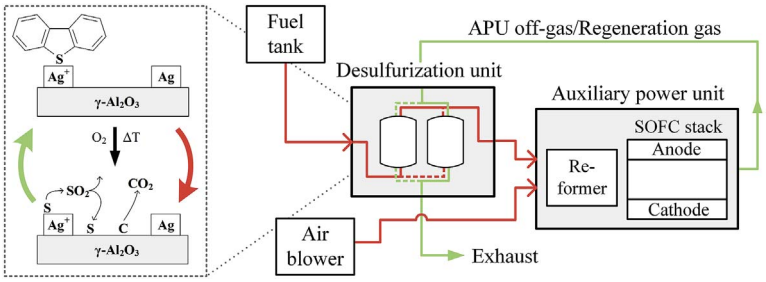
HIGHLIGHTS

- Efficient adsorptive desulfurization at −10 to < 60 °C using Ag-Al_2O_3 as adsorbent.
- In situ adsorbent regeneration via hot APU off-gas.
- Thermal and chemical stability of Ag-Al_2O_3 under APU off-gas conditions.
- Constant desulfurization and regeneration performance over multiple cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

On-board desulfurization is essential to operate fuel-cell-based auxiliary power units (APU) with commercial fuels. In this work, both (i) on-board desulfurization and (ii) on-board regeneration performance of Ag-Al_2O_3 adsorbent is investigated in a comprehensive manner. The herein investigated regeneration strategy uses hot APU off-gas as the regeneration medium and requires no additional reagents, tanks, nor heat exchangers and thus has remarkable advantages in comparison to state-of-the-art regeneration strategies. The results for (i) show high desulfurization performance of Ag-Al_2O_3 under all relevant operating conditions and specify the influence of individual operation parameters and the combination of them, which have not yet been quantified. The system integrated regeneration strategy (ii) shows excellent regeneration performance recovering 100% of the initial adsorption capacity for all investigated types of fuels and sulfur heterocycles. Even the adsorption capacity of the most challenging dibenzothiophene in terms of regeneration is restored to 100% over 14 cycles of operation. Subsequent material analyses proved the thermal and chemical stability of all relevant adsorption sites under APU off-gas conditions. To the best of our knowledge, this is the first time 100% regeneration after adsorption of dibenzothiophene is reported over 14 cycles of operation for thermal regeneration in oxidizing atmospheres.

1. Introduction

On-board desulfurization is mandatory to operate highly efficient but sulfur sensitive fuel cell systems with commercial hydrocarbon-based fuels in mobile applications. The total sulfur content in commercial fuels is in the range of 10–5000 ppm and depends on the type of

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fuel and the correlated legal requirements [1]. Hydrodesulfurization (HDS) is the most prevalent and industrially relevant desulfurization technology for petroleum-based fuels. The HDS process is a catalytic process with high operating temperature (300–400 °C) and pressure (3–6 MPa) in the presence of H_2 [2,3]. In this process the conversion rate significantly decreases with increasing size of the polycyclic aromatic sulfur heterocycles (PASHs) [2]. Consequently, benzothiophene (BT) and its derivatives, as also dibenzothiophene (DBT) and its derivatives are the typical PASHs present in gasoline and jet fuel, as also in diesel fuel, respectively [2,4].

Fuel cell systems are one of the most efficient tools for converting chemical into electrical energy. This technology simply converts hydrocarbon-based fuels into hydrogen-rich syngas via reforming, which is then fed to e.g. a solid oxide fuel cell (SOFC) [5–7]. This system is very attractive for auxiliary power units (APUs) for trucks, ships, or airplanes since it eliminates the challenges of additional hydrogen storage [8]. All these reported systems require a desulfurized fuel [8,9] in order to protect the reformer catalyst and the fuel cell electrodes which have a sulfur threshold limit of < 50 and 1 *ppmw* of total sulfur, respectively [4,10–12].

Several on-board desulfurization techniques have been studied and reported in recent years. For example, Wang et al. [13] reported an on-board desulfurization unit based on hydrodesulfurization. The reported results are promising but extensive equipment and additional hydrogen is needed. Desulfurization via adsorption is very attractive for on-board applications, in particular due to its simplicity. A wide range of different adsorbents were investigated [1,14,15]. However, the reported breakthrough adsorption capacity for real fuels is only in the range of 0.22–25.3 *mg/g* [16,17] and is thus too low for continuous APU operation over several days. Consequently, efficient adsorbent regeneration has become a main target in recent years.

When it comes to on-board regeneration, only thermal regeneration strategies in oxidizing atmospheres are reasonable. Other approaches, such as solvent-based regeneration or thermal regeneration in reducing atmospheres (N_2, H_2, or He) would require additional tanks and solvents/gases and are thus not reasonable [18]. Hence, most of the promising adsorbents such as Cu or Ni-based ones are excluded for on-board applications as these adsorbents need activation in reducing atmospheres [16,19,20]. In addition, carbon-based adsorbents are also inefficient as these adsorbents are not stable under an oxidizing atmosphere at higher temperatures (> 400 °C) which are essential for efficiently decomposing PASHs during regeneration [21–23].

Silver-based adsorbents are reported to work in the oxidized form [24,25]. The overall adsorption mechanisms of silver incorporated metal oxides include two interactions of the sulfur heterocycles with the active silver phase, and one involving the acidic surface groups of the metal oxide support (e.g. Al_2O_3) [26–28]. The two stronger interactions involving the active silver phase are based on a π-complexation (referred to as π-Ag interaction) and a direct metal sulfur interaction (referred to as S-Ag interaction). The weak adsorption mechanism involving the acidic surface group is based on an acid base interaction and is thus referred to as S-H interaction. A more detailed discussion about the adsorption mechanisms related to Ag-Al_2O_3 can be found elsewhere [26]. Results for Ag-SiO_2, Ag-TiO_2, and Ag-MCM-41 for example showed high adsorption capacities for different types of PASHs [25,29,30]. However, fundamental investigation on the influence of adsorption temperature, type of fuel, and type of PASH has not yet been studied. This investigation is not only necessary in order to study the influence from the scientific point of view but also to quantify the desulfurization performance under realistic conditions. For example, Song et al. [31] reported an optimal adsorption temperature of 50 °C for a AgCeY zeolite desulfurizing a model fuel containing thiophene or BT. However, the influence of different types of real fuels and thus different types and concentrations of aromatic hydrocarbons on the adsorption performance has not been investigated. At the same time, several authors reported significant influence on the adsorption capacity by the type of fuel where the magnitude strongly depends on the type of adsorbent [32,33]. For example, Ma et al. [34] reported good desulfurization performance of a Ni-based adsorbent for gasoline and jet fuel but not for diesel fuel. This effect was related to the adsorption mechanism having insufficient selectivity towards PASHs in the presence of polycyclic aromatic hydrocarbons (PAHs). These PAHs have similar molecular structures in comparison to PASHs and thus compete for adsorption. Table 1 shows the typical contents of monoaromatics and PAHs of commercial jet and diesel fuel.

Table 1
Typical content of monoaromatics and polycyclic aromatic hydrocarbons (PAHs) in jet and diesel fuel.

Fuel	Monoaromatics	PAHs
Jet fuel[a]	15 - 25 *vol.%*	0.1–1.7 *vol.%*
Diesel fuel[b]	15 - 25 *wt.%*	4 - 10 *wt.%*

[a] Ref. [35–37].
[b] Ref. [33,38].

The high content of PAHs in diesel fuels increase the challenge of efficient adsorptive desulfurization. The selectivity of the adsorbent towards PASHs in the presence of PAHs is thereby strongly influenced by the adsorption temperature. In order to quantify reasonable adsorption performances, the investigation of all influence parameters and the combination of them in a comprehensive manner is indispensable, since the parameters strongly affect each other.

As mentioned above, silver-based adsorbents are active in the oxidized form and thus allow thermal regeneration in an oxidizing atmosphere without subsequent activation. This fact makes silver-based adsorbents very attractive for on-board desulfurization units. Ambient air was used as the regeneration medium in a number of studies which investigated thermal regeneration of silver-based adsorbents. The reported results are promising but in all experiments a degradation of the breakthrough capacity was observed within 2–5 cycles [30,32,39]; only Wang et al. [40,41] reported full regeneration over 70 cycles for a Al_2O_3-based adsorbent with metallic promoters (not further specified). These 70 cycles of operation were carried out with a light fraction of jet A-1 (no DBT) using ambient air as regeneration medium at 500 °C. In all these mentioned studies, regeneration performance was always investigated after desulfurization of gasoline or jet fuel containing thiophene, BT, or their derivatives as sulfuric compounds. This is an important fact to mention, since all recently published articles dealing with thermal regeneration in ambient air after adsorption of DBT report a degradation of the adsorption performance within the first 3 cycles [22,42,43]. This phenomenon is related to the fact that thiophene, BT, and their derivatives have a lower adsorption energy and chemical stability in comparison to DBT [2,26,27]. In addition, derivatives of DBT, such as 4,6-dimethyldibenzothiophene, have also a lower adsorption energy, since the methyl and ethyl substituents lower the electron density on the S atom [26,27,44]. Consequently, DBT is the most challenging PASHs in terms of regeneration and full thermal regeneration in ambient air has never yet been reported to the best of our knowledge; neither for silver-based adsorbents nor for any other adsorbents.

In this study, both (i) on-board desulfurization and (ii) on-board regeneration performance of Ag-Al_2O_3 was investigated in a comprehensive manner including variations of adsorption temperature, type of fuel, type of PASH, combinations of them, and a novel system integrated regeneration strategy. This system integrated regeneration strategy uses hot APU off-gas from an SOFC operated auxiliary power unit as the regeneration medium. A flow sheet of this novel regeneration approach is illustrated in Fig. 1. With this system integrated regeneration strategy, multiple cyclic use over 14 cycles of operation were carried out to investigate the long term desulfurization performance and the chemical and thermal stability of Ag-Al_2O_3.