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Oxygen impurity in nitrogen desorption purge gas can increase heel buildup on activated carbon

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A B S T R A C T

Heel formation during cyclic adsorption/regeneration of volatile organic compounds (VOCs) on activated carbon decreases its adsorption capacity and lifetime. The effect of regeneration purge gas oxygen content on activated carbon performance, specifically during successive adsorption/regeneration cycles was investigated. 5-cycle adsorption/regeneration tests were performed on a microporous activated carbon using 1,2,4-trimethylbenzene (TMB) as adsorbate. Nitrogen with different oxygen concentrations (≤5, 208, 625, 1250, 2500, 5000, 10,000, and 20,000 ppm_v) was used as regeneration purge gas during thermal desorption of TMB (at 288 °C). Cumulative heel formation increased from 0.5% to 15.8% as the oxygen concentration in the desorption purge gas increased from ≤5 to 20,000 ppm_v. Thermogravimetric analysis of the regenerated samples showed extensive chemisorption of TMB when exposed to ≥625 ppm_v oxygen in the purge gas. The results suggest that regeneration purge gas oxygen impurity can increase heel formation, resulting in lower regeneration efficiency and shorter adsorbent lifetime. The results from this study help explain the heel formation mechanism and how it is related to regeneration purge gas purity.

1. Introduction

Adsorption on activated carbon is an established method for capturing volatile organic compounds (VOCs) from industrial gas streams [1–3]. Adsorption is typically followed by regeneration to allow reuse of the adsorbent [1,3,4]. Thermal desorption at temperatures of < 300 °C is industrially used for regeneration of adsorbents loaded with gas phase compounds [1,2].

Ideal regeneration will remove all of the adsorbed species from the adsorbent, however, in reality some of the adsorbates remain inside the adsorbent pores after regeneration. These residual compounds are defined as heel. Heel buildup is a challenge during regeneration of activated carbon over multiple cycles, since it reduces its adsorption capacity and lifetime [5–8]. Previous studies have extensively investigated heel formation mechanisms in the aqueous phase [5,7–10], and to some extent in the gas phase [1,2,11–17]. In gas phase studies, the effect of adsorption temperature [16], regeneration temperature [2,12,16], adsorbent porosity [13], adsorbent surface functional groups [14], purge gas oxygen impurities [1,11], adsorption bed configuration (fixed versus fluidized bed) [15], and competitive adsorption between the VOC species [17] on heel formation were studied. Heel formation mechanisms include non-desorbed physisorption [18], chemical adsorption [19], oligomerization [7], and adsorbate decomposition [20].

During regeneration, gas is purged through the adsorbent bed to help remove the desorbed species and prevent combustion. Desorption at high temperatures and high VOC concentrations requires an inert purge gas to prevent bed fires and combustion [1]. However, for low temperature regeneration and low VOC concentration, air is used as desorption purge gas [11]. The type of purge gas used for regeneration can affect not only heel formation, but also the cost of operation. The use of high purity N_2 as the regeneration purge gas is common both in research and in industrial applications [2,21,22]. Impurities in the purge gas may affect the regeneration efficiency. These impurities are mainly oxygen; however, traces of CO_2 and H_2O may also be present [1]. Presence of oxygen even at very low concentrations may increase heel formation as it triggers chemical reactions with the adsorbate and/or adsorbent at elevated temperatures [1,23].

Previous researchers have investigated the effect of oxygen in the purge gas to a limited extent. Carratala et al. [11] studied adsorption and desorption of benzene and phenol on five different activated carbons. Regeneration was performed at 250–350 °C in an inert atmosphere (He) and an oxygen containing atmosphere (20% O_2 in He) to compare regeneration efficiencies. They observed that benzene and toluene adsorption capacities remained unchanged after successive helium regeneration cycles for all activated carbons, while regeneration in the presence of oxygen gradually reduced the adsorption capacity for

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certain activated carbons due to the presence of potassium salts (carbon gasification catalysts from their activated carbon preparation procedure). They attributed this reduction to porosity modification and increase in surface oxygen groups [11].

Jahandar Lashaki et al. [1] adsorbed a mixture of volatile organic compounds on activated carbon and regenerated the carbon at 288 °C using nitrogen purge gas with different levels of oxygen content (from ≤5 ppm_v to 10,000 ppm_v). They observed that heel formation after five successive cycles was increased at higher O_2 concentrations (from 19.5% to 25.6% for ≤5 ppm_v to 10,000 ppm_v). They attributed heel formation to a combination of physisorption and chemisorption (suggested mainly by the stronger forces of attraction resulting in a higher desorption temperature), the latter being the dominant mechanism at higher O_2 concentrations. They also investigated the effect of long-term exposure (50-cycles) of samples to purge gas oxygen and observed that at a high O_2 concentration (5000 ppm_v) chemisorption was the main heel formation mechanism, in agreement with the short-term exposure results, while no evidence of chemisorption was observed at a lower O_2 concentration (50 ppm_v) [1]. However, the extent to which each compound in the mixture contributes to heel formation was not studied. In order to do so, single component adsorption/regeneration tests must be carried out to see their effect, individually, on heel formation. In the present work, we tried to gain insight into the role of a single compound, namely 1,2,4-trimethylbenzene, in heel formation.

There is little to no data available on the effect of purge gas oxygen content on adsorption and regeneration of single adsorbates at impurity-type concentrations. Therefore, studying the effect of oxygen content in the purge gas at levels commonly found in industrial applications on adsorption and regeneration of single adsorbates is significant. Using a single adsorbate, instead of a mixture, allows isolating the specific heel formation mechanism that might be confounded with other mechanisms when using a mixture. This paper investigates the regeneration of beaded activated carbon (BAC) saturated with a TMB-laden air stream using nitrogen purge gas containing different levels of oxygen impurity. The effect of oxygen content in the purge gas was investigated by quantifying heel formation and characterizing the regenerated BAC samples.

2. Materials and methods

2.1. Adsorbent and adsorbate

Beaded activated carbon (BAC; G-70R; Kureha Corporation) was used as the adsorbent for all experiments. The BAC has high microporosity (88%), narrow particle size distribution (average particle diameter 0.70 mm, 99% mass between 0.60 and 0.84 mm), and very low ash content (< 0.05%) [24]. BAC was preheated at 200 °C for 2 h before use to remove adsorbed impurities. 1,2,4-trimethylbenzene (TMB, 98%, Acros Organics) was used as adsorbate for all experiments. TMB was selected as a surrogate for aromatic compounds typically found in automotive paint solvents [17]. In addition, previous studies have showed its tendency to result in heel buildup on activated carbon [1,2,16]. TMB has a high boiling point (171 °C) and a large kinetic diameter (0.61 nm [25]) and thus tends to fill up the narrow micropores (< 0.8 nm) during adsorption.

2.2. Experimental setup and methods

The experimental setup is described in detail elsewhere [1] and is briefly described here (Fig. 1). The setup consists of an adsorption/regeneration tube, an adsorbate generation system, a heat application module, a gas concentration measurement system, and a data acquisition and control (DAC) system. The adsorption/regeneration setup is a stainless-steel tube filled with 4.0–4.1 g of BAC. Glass wool was used at the top and bottom of the tube to provide support for the BAC. The temperature was maintained at 23 ± 2 °C during adsorption. A K-type

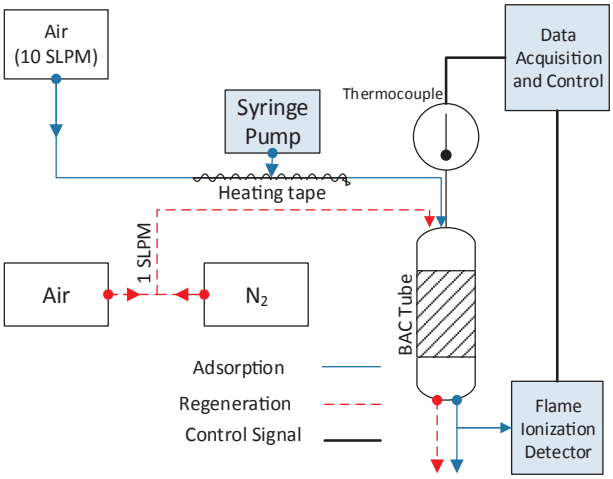

Fig. 1. Schematic of the adsorption/regeneration setup.

thermocouple was used to control the temperature of the adsorbent bed during adsorption and regeneration. The adsorbate was injected into a dry air stream of 10 SLPM (standard liters per minute) using a syringe pump, generating a VOC concentration of 500 ppm_v. The outlet concentration during adsorption was intermittently measured using a flame ionization detector (FID; Baseline-Mocon Inc. series 9000) to obtain breakthrough curves. Adsorption experiments were carried out for 2 h to allow saturation of the adsorbent.

Regeneration of the adsorbent was performed at 288 °C (550 °F) to simulate industrial operational conditions [26] and allow for desorbing of adsorbed species, while minimizing energy consumption and potential damage to the adsorbent structure due to exposure to high temperature [3].

Heat was provided using a heating tape wrapped around the adsorption/regeneration tube, surrounded by a wrap of insulation tape to minimize heat loss. The regeneration temperature was controlled using a DAC system with a LabVIEW program (National Instruments) and a data logger (National Instruments, Compact DAQ) equipped with analog input and output modules. During regeneration, the adsorption/regeneration tube was heated for 3 h after which heating was stopped and the tube was allowed to cool to room temperature. During regeneration and cooling, the adsorbent bed was purged with 1 SLPM (standard liters per minute) total flow of gas, containing nitrogen with different levels of oxygen impurity (≤5, 208, 625, 1250, 2500, 5000, 10000, and 20,000 ppm_v). Ultra-high purity nitrogen (grade 4.8, 99.9984% pure, Praxair) was mixed with air (99.999% pure, Praxair) using a 1 SLPM mass flow controller (Alicat Scientific) for N_2 (accuracy of ± 0.003 SLPM) and a 100 ± 0.3 SCCM (standard cubic centimeters per minute) mass flow controller (Alicat Scientific) for air. The ultra-high purity N_2 contained a maximum of 5 ppm_v O_2 and was used by itself as the purge gas for the ≤5 ppm_v O_2 experiments.

Two blank, five-cycle adsorption-regeneration experiments were also conducted to determine the effect of purge gas oxygen content on adsorbent properties in the absence of adsorbate (i.e., TMB). To that end, adsorption cycles were completed by purging the adsorption bed with TMB-free air. Afterwards, regeneration was carried out at 288 °C using oxygen levels of ≤5 ppm and 20,000 ppm in the purge gas.

Heel formation and adsorption capacity were quantified using gravimetric analysis and are reported as percentages relative to the initial BAC weight. The difference between the weight of the tube before and after each adsorption cycle represents the amount of VOC adsorbed during that adsorption cycle. The difference between the weight of the tube after the last regeneration cycle and before the first adsorption cycle weight represents the cumulative heel. Finally, the difference in cumulative heel between two regeneration cycles represents the amount of heel formed during the latter regeneration cycle.