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Selective dielectric heating for efficient adsorptive-catalytic cleaning of contaminated gas streams

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ABSTRACT

A dynamic phenomenon of selective dielectric heating using radio-frequency energy is used to establish a continuous process for the elimination of organic pollutants from contaminated gas streams. The process consists of two phases characterized by adsorption and by regeneration utilizing in situ catalytic oxidation. The thermal regeneration of the packed bed is started by a so-called thermo-chromatographic pulse, i.e. a combined water/temperature pulse moving through the reactor with a packed bed containing both an adsorber and a catalytically active component (NaY zeolite and Pt, respectively). The pronounced temperature pulse is formed due to the strongly enhanced absorption of electromagnetic energy within a water pulse. This can be explained by the complex dependency of the energy absorption on both local moisture content and local temperature of the zeolite. As a result, the previously adsorbed organic contaminants are desorbed and, simultaneously, the catalyst is thermally activated leading to total oxidation of the released hydrocarbons. Thus, the gas stream can be permanently cleaned employing only one packed bed reactor. This has been demonstrated for various experimental conditions.

1. Introduction

The continuous cleaning of contaminated gas streams is a prevalent issue in environmental technology. Hazardous compounds such as volatile organic compounds (VOC) and namely organic solvents or odorous compounds can originate from many industrial or agricultural processes (use of paints and varnish, chemical production, stock breeding) [1–5] or even processes in environmental technology such as soil or groundwater remediation by soil vapour extraction or stripping techniques [6,7]. Although a number of established methods for gas treatment are available, there is still a technological and efficiency gap for mean or fluctuating concentrations. For gas streams with low hydrocarbon contents, adsorption on activated carbon or on hydrophobic zeolites [5,8–10] can be applied and it usually works economically. For higher concentrations of organic pollutants, thermo-catalytic oxidation [11–13] can be utilized because the combustion heat of the hydrocarbons can be used to maintain the working temperature of the catalyst and, if necessary, to preheat the gas flow. However, for situations with mean carbon contents in the range from 0.1 to 2 g carbon (gC) per cubic metre or with varying concentrations, a flexible and efficient clean-up technology is often still missing.

These critical conditions are in the focus of the new concept presented here which can be characterized by a combination of adsorption and regeneration by thermo-catalytic oxidation initiated by selective dielectric heating. In the adsorption phase performed at low temperature, the contamination is eliminated from the gas stream by adsorption on a zeolite, in the case presented here, NaY. The system is operated in this mode until the maximum adsorption capacity of the packed bed is reached. Before the hazardous compounds can be detected in the effluent from the reactor, the regeneration phase is started by heating. The catalytically active component is present together with the adsorbent in the same packed bed. Two possible options for such a material acting both as collector and catalyst were tested in the present study. In one case, a noble metal was supported on the porous zeolite, and in the second case, a metal-containing alumina was mechanically mixed with the zeolite.

The regeneration temperature was established by dielectric heating using radio-frequency (RF) energy [14]. This method has some advantages in comparison to conventional heating by the gas stream or by an external furnace. Due to the relatively low heat capacity of the purge gas stream, heating via the gas flow would lead to low heating rates and an undesired dilution of the desorbing pollutants. External heating across the reactor walls results in large temperature gradients within the packed bed due to the low thermal conductivity of the granular packing. In contrast, dielectric heating is generally characterized by direct energy transfer into

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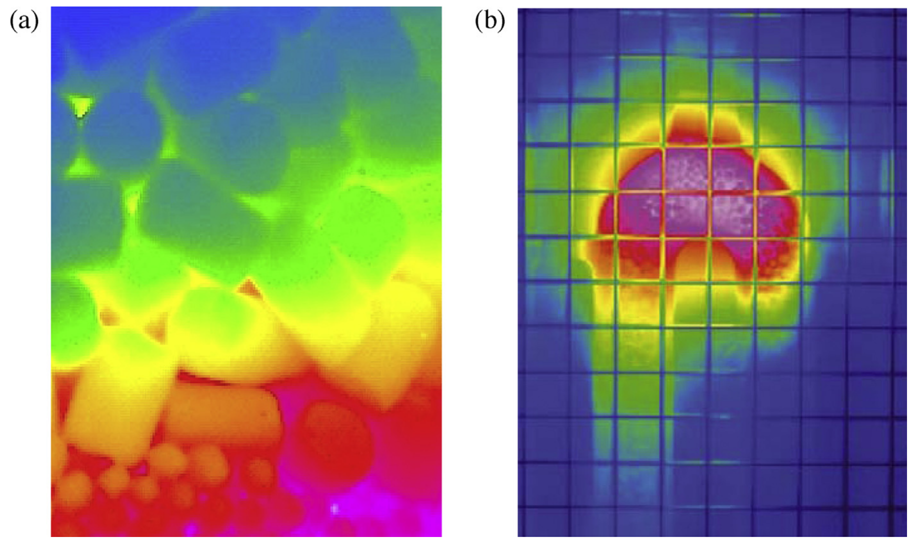

Fig. 1. Infrared image demonstrating selective dielectric heating of zeolites with radio waves (frequency 13.56 MHz): (a) layered arrangement of zeolites NaX (small particles, about 150 °C) and dealuminated Y (DAY, large particles, about 45 °C) and (b) thermo-chromatographic pulse (TCP) in a packed bed of zeolite NaY (hot zone with temperatures around 200 °C).

the volume of the solid material. Neither a heat transfer medium nor overheated surfaces are necessary and heating is not limited by the internal heat flow. Based on these advantages, dielectric heating applying electromagnetic waves with frequencies of some GHz (microwaves [MW]) or MHz (radio waves [RW]) have been introduced for temperature-swing adsorption techniques [14–18].

Compared to MW, RW usually have markedly larger penetration depths which leads to a much better homogeneity of heating especially in the technical scale (some litres or cubic metres). Additionally, RF heating of zeolites does not depend on the presence of water and a wide spectrum of materials including hydrophobic or hydrophilic zeolites can be efficiently heated [14,19]. The energy absorption in the RF range is mainly due to the migration of structural cations within the zeolite framework. The corresponding relaxation processes are influenced by the moisture content but not solely depending on it [20–26]. Thus, zeolites with a wide variety of adsorptive and catalytic properties are accessible to dielectric heating when RW are employed.

In addition to RF heating of zeolites or other adsorbents and catalysts in the context of chemical engineering, off-gas treatment and drying of biogas and natural gas [27], dielectric heating with RW has been successfully applied for various other materials in the technical scale. Examples for application options are in situ RF heating of contaminated dry or moist soil for thermally enhanced remediation [6,7,28–30], of timber for pest control and of wooden constructions, stone or concrete for enhanced drying or thermally supported decontamination [31]. In general, a wide spectrum of dry and moist non-conducting materials is accessible to RW heating and, therefore, this technique is more flexible compared to the more established MW heating.

Besides the potential to achieve homogeneous heating of large-scale packed beds, RF heating also provides the chance to realize selective heating of distinct components in a complex system. In this case, the specific energy absorption characterized by the imaginary part of the dielectric constant, the so-called dielectric loss factor, is the relevant property severely varying for different types of zeolites [14,20–22]. This could be exemplarily demonstrated for a layered arrangement of NaX and dealuminated Y zeolites where overheating of NaX by more than 100 K was observed [23] (Fig. 1a).

Another option for realizing selective heating is the introduction of a coupling medium significantly enhancing the dielectric loss factor of the material exposed to the electromagnetic field. One illustrative example for this phenomenon is the effect of water on the dielectric heating of zeolite NaY. Interestingly, the dielectric loss factor of this zeolite becomes maximal at mean water contents in the range of 3 wt.% [24]. The complex dependency of dielectric RF heating on the moisture content and the temperature of this zeolite is the basis of a so-called thermo-chromatographic pulse (TCP). When water is introduced at the inlet of a NaY packed-bed reactor being under the influence of the RF field, the temperature in the first zeolite layer increases significantly. As a result of the high temperature obtained, the adsorbed water starts to desorb and is transported by the gas stream to the next, colder section of the zeolite bed. There, it is adsorbed and the increase of the water content corresponds to enhanced energy absorption. This again leads to strong dielectric heating. The resulting successive adsorption/desorption cycles lead to a migrating water/temperature pulse continuously moving through the zeolite packed bed (Fig. 1b). Finally, a focussed water pulse is leaving the packed bed reactor and the temperature is decreasing again [25,26]. The analogy of this process to gas chromatography was the origin of the denotation as TCP.

The TCP as a special example of selective dielectric heating with RW was used in the frame of a new concept to initiate the thermal regeneration of the loaded adsorber bed. The temperature pulse fulfils two different functions: First, it leads to the thermodesorption of the hydrocarbons adsorbed in the previous process phase. Secondly, the temperature increase leads to the activation of the metal catalyst. Thus, the desorbed organic pollutants are directly oxidized in the packed-bed reactor forming CO_2 and water (and HCl in case of chlorinated compounds).

This new concept of an adsorptive-catalytic gas cleaning would allow a continuous purification with only one packed-bed reactor. Due to the total oxidation as inherent step, no subsequent gas treatment is necessary. Using the TCP instead of heating the whole reactor bed also decreases the energy consumption. The demonstration of this innovative concept for different conditions is the objective of this paper.