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Purification of landfill biogases from siloxanes by adsorption: A study of silica and 13X zeolite adsorbents on hexamethylcyclotrisiloxane separation

Tania Montanari[a], Elisabetta Finocchio[a,*], Irene Bozzano[a], Gilberto Garuti[b], Andrea Giordano[b], Chiara Pistarino[c], Guido Busca[a]

[a] Dipartimento di Ingegneria Chimica e di Processo, Facoltà di Ingegneria, Università di Genova, Pl.e Kennedy 1, I-16126 Genova, Italy
[b] Acqua e Sole S.r.l., Milano, Italy
[c] Ecodeco S.p.A., Cassinazza di Baselica, 27010 Giussago PV, Italy

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ABSTRACT

The adsorption capacity on and the desorption from pure activated carbons, silica and NaX zeolite, of hexamethylcyclotrisiloxane (HMCTS or D_3, a common siloxane impurity in biogases) has been evaluated in laboratory experiments using synthetic biogas. The adsorption mode of this molecule has also been investigated by FT-IR spectroscopy. HMCTS adsorbs on silica by hydrogen bonding on the surface hydroxyl groups. However, its desorption up to 200 °C by purging with nitrogen as well as by vacuum treatment, is incomplete, leaving surface hydroxyl groups partially affected. Limited desorption is observed also from activated carbons at temperatures between 20 and 200 °C. On zeolite NaX molecular adsorption as well as reactive adsorption occurs, partial desorption being obtained by purging with nitrogen already at room temperature. In the three adsorbents, polymerization of HMCTS to silicone is found during adsorption in dynamic conditions. This is supposed to be the common cause of the only partial regenerability of all these solids after HMCTS adsorption.

1. Introduction

Biogases are methane and carbon dioxide rich mixtures produced by anaerobic digestion of several waste materials such as sewage sludge, animal manure and landfill wastes. Biogases may be upgraded to methane-rich fuel gas, burnt as such to produce heat, used as fuels of spark ignition engines or gas turbines to recover electricity or combined heat and power, used as a fuel of direct biogas fuel cells or converted to syngas or hydrogen by steam reforming of methane to feed hydrogen fuel cells [1].

The application of biogases is hampered by the presence of several impurities, such as sulphide, halide and polysiloxane compounds. Siloxanes, which mostly arise from hydrolysis of polydimethylsiloxanes used in several industrial and household applications [2], represent troublesome impurities for biogas upgrading equipments [3–6]. In fact, they decompose upon biogas burning producing fine silica powders which damage rapidly the pistons of spark ignition engines and vanes of gas turbines. Siloxanes also depose on steam reforming catalysts and FC anodes, causing their silication and consequent deactivation. The presence of siloxanes makes also more complex the issue of purification of biogases from sulphide and halide compounds.

Several techniques have been developed, also at the industrial level [7,8], to purify biogases from siloxanes, such as condensation, absorption in liquids, adsorption on solids at room temperature and decomposition. High temperature treatment with solids, such as alumina [9], has been found to allow complete siloxane removal. This technique can indeed be applied to treat biogases prior to steam reforming and/or to utilization with high temperature fuel cells [10], waste heat produced by the fuel cell being used to preheat the landfill gas. On the other side, this technique, where the silicate adsorbent cannot be regenerated, cannot be applied to energy generation with spark ignition engines. Biological removal of siloxanes is also possible but is very slow, thus posing significant challenges [11].

Room temperature adsorption on porous solids represents the most common practice today to abate such compounds. The most efficient solids to remove siloxanes are activated carbons (ACs) [12–14]. However, according to both landfill gas treatment practice and laboratory experiments [12,15], ACs can only be partially regenerated from siloxanes after use. This makes the cost of the adsorbent quite significant. Although several patents have been issued claiming the development of regenerable adsorbents for siloxanes (see the review of Ajhar et al. [8]) this seems to be in practice still an unsolved problem.

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* Corresponding author. Tel.: +39 010 3536027; fax: +39 010 3536028.
E-mail addresses: tania.montanari@unige.it (T. Montanari), elisabetta.finocchio@unige.it (E. Finocchio), gilberto.garuti@belleuropa.net (G. Garuti), c.pistarino@ecodeco.it (C. Pistarino), guido.busca@unige.it (G. Busca).

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Table 1
Adsorption and desorption capacities for HMCTS over solids.

Adsorbent	Supplier and type	Apparent density (g/mL)	BET surface area (m^2/g)	Effective adsorption capacity (g_{HMCTS}/g_{ADS})	Desorbed/adsorbed HMCTS
Silica Gel	Grace	0.72	350	0.230	0%
Faujasite NaX	Sylobead MS 544 Grace	0.69	500	0.276	16% at 100 °C 23% at 200 °C
Pure activated carbon	NORIT RB4	0.41	>1000	0.580	4% at 100 °C 8% at 200 °C

Other solids are reported to be active in siloxane adsorption. In particular, Schweigkofler and Niessner [3] tested inorganic materials like silica and 13X molecular sieve. These authors concluded that silica may be a cost effective and efficient solution, although its regeneration needs heating and was reported to be incomplete. Also Matsui and Imamura reported silica to act as a quite efficient adsorbent for siloxanes, but less than some ACs [14].

Among siloxanes detected in biogases, the linear dimeric hexamethyldisioxane (L2) and the cyclic trimeric hexamethylcyclotrisiloxane (HMCTS, D3) and tetrameric octamethylcyclotetrasiloxane (D4) are usually the most abundant. However, the concentration of impurities in biogases is very sensitive to conditions (temperature, moisture content, age of loading and so on) and fluctuates very much with time. In the present paper we will report some of the results we obtained concerning the separation of hexamethylcyclotrisiloxane (HMCTS), one of the common siloxanes present in landfill biogases, and sometimes the most abundant, whose volatility is intermediate among the most abundant ones, which we used in previous studies [9,12]. HMCTS was separated from synthetic biogases using silica and 13X molecular sieve. The results obtained are discussed in comparison to those obtained by an activated carbon which demonstrated excellent adsorption properties but only partial regenerability both in lab experiments and on-field practice.

2. Materials and methods

Data on the materials used as adsorbents are summarized in Table 1. For the skeletal analysis of the fresh and spent adsorbents (Figs. 1 and 2) powders diluted in KBr pressed disks were used (0.1% w/w).

Hexamethylcyclotrisiloxane (HMCTS) was purchased from Aldrich. Flow adsorption tests have been performed at room temperature and atmospheric pressure as reported previously [12] using a tubular quartz reactor (30 cm long, 0.6 cm internal diameter), where a fixed bed of 1.3 g of adsorbent material in pellets was fixed with glass wool. The adsorbents were exposed to a synthetic biogas (CO_2/CH_4, 45/55% v/v, purchased from SIAD) saturated at room temperature with HMCTS (corresponding to about 5 mg/min) and water vapour by bubblers (25 °C). Total flow rate was 60 ml/min, corresponding to a contact time around 2 s calculated using the apparent bed volume of powdered pellets. Although HMCTS is far larger than the typical one for landfill biogases, conditions were set in order to allow short adsorbent screening experiments.

Analyses of the gaseous flows have been performed by on line FTIR (ThermoFisher Nicolet 6700) equipped with a gas cell connected to the adsorption apparatus and operating with OMNIC^{TM} Series acquisition software. This analysis allows to obtain a complete IR spectrum in the Mid IR range every 4 s, thus monitoring continuously the trends of the diagnostic siloxane, CO_2, methane and water IR bands (Fig. 3). The effective siloxane adsorption capacities of the materials have been determined by evaluating the time-on-stream at 100% siloxane removal before breakthrough (Fig. 4). The quantitative analysis of HMCTS in the biogas was obtained by following the intensity of the bands at 1035 cm^{-1} and/or at 818 cm^{-1}. For methane the rotovibrational components around the CH_4 asymmetric stretching mode were taken as diagnostic, while for CO_2 the overtones in the region

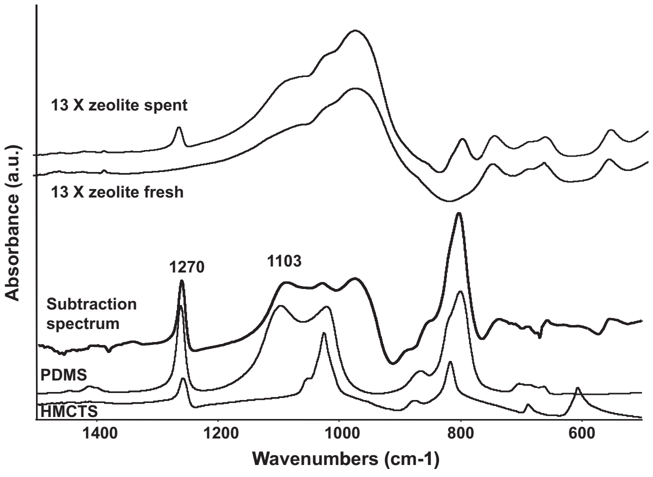

Fig. 1. FT-IR spectra of KBr pressed disks of zeolite 13 X fresh and spent after adsorption runs on treatment of synthetic biogas with HMCTS, as well as of solid HMCTS and of a polydimethylsiloxane (PDMS) film reported as reference. Subtraction spectrum = [spent 13X spectrum] − [fresh 13X spectrum].

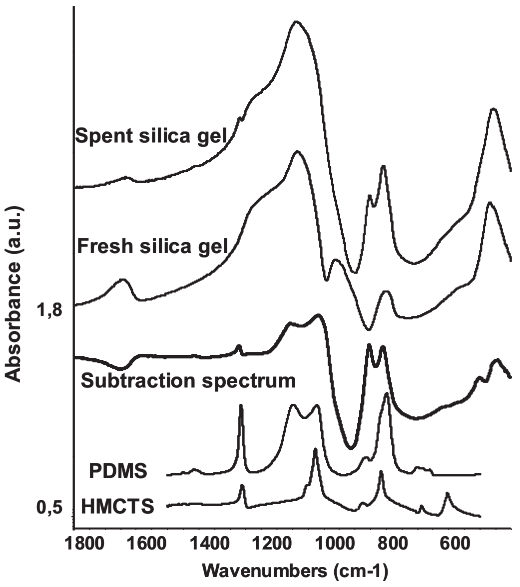

Fig. 2. FT-IR spectra of KBr pressed disks of silica gel fresh and spent after adsorption runs on treatment of synthetic biogas with HMCTS, as well as of solid HMCTS and of a polydimethylsiloxane (PDMS) film as reference. Subtraction spectrum = [spent silica gel spectrum] − [fresh silica gel spectrum].

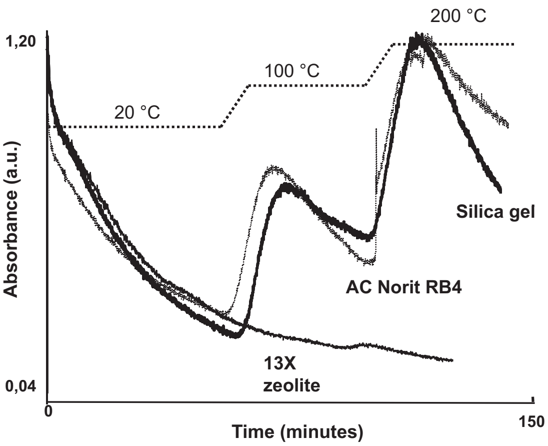

Fig. 3. Behavior of the IR diagnostic band of gaseous HMCTS flowing in the IR cell during purging adsorbent beds previously saturated by HMCTS upon adsorption of synthetic biogas. Broken line: the heating cycle.

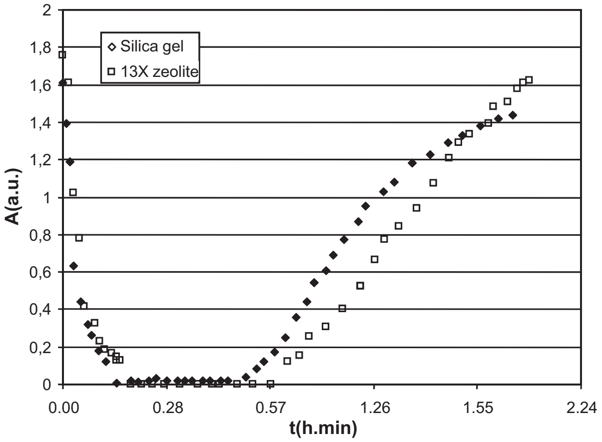

Fig. 4. Behavior of the concentration of HMCTS in the synthetic biogas flowing out of the adsorption column for silica gel and 13X zeolite at room temperature and in the presence of water vapour.

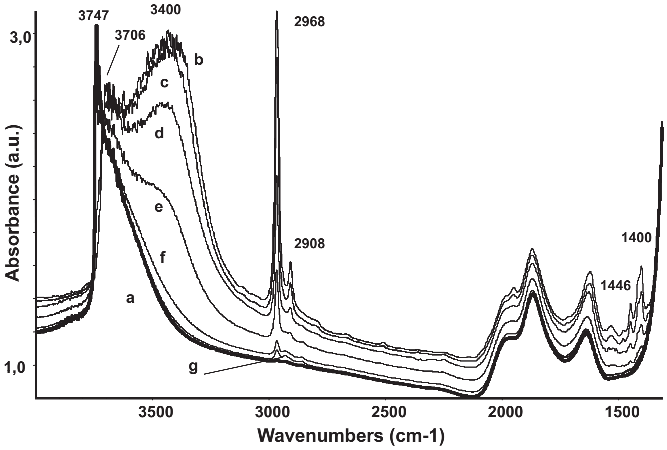

Fig. 5. FT-IR spectra of silica gel pressed disk after outgassing at 400 °C (a), after subsequent contact with HMCTS vapour (gas phase spectrum subtracted) (b), and following outgassing at r.t. 10 min (c), at r.t. 1 h (d), at 60 °C 10 min (e), at 150 °C 10 min (f), at 200 °C 10 min (g).

3800–3600 cm^{-1} were taken as diagnostic, in order to avoid signal saturation occurring with the most intense bands. For water we used the rotovibrational components around the H_2O bending mode.

Using the same apparatus, the desorption of siloxane was studied. After saturation of the adsorbent, pure nitrogen flow was switched on the column and the IR cell. The column was kept under flowing nitrogen at room temperature for 40 min, then heated at 10 °C/min to 100 °C, left 40 min, then heated again at 10 °C/min to 200 °C and left 40 min. During this time, continuous analysis of the downstream gas was done by FT-IR.

Spectroscopic adsorption experiments (Figs. 5–7) were performed in static conditions, using a conventional manipulation/outgassing ramp connected to the IR cell. Pressed disks of pure adsorbent powders (15 mg, 1 cm diameter) were used. IR spectra were recorded with a Nicolet Nexus Fourier Transform instrument. The samples were thermally pre-treated in the IR cell by outgassing 1 h at 400 °C. The adsorption procedure involves contact of the activated sample disk with HMCTS vapour at r.t. in the conventional

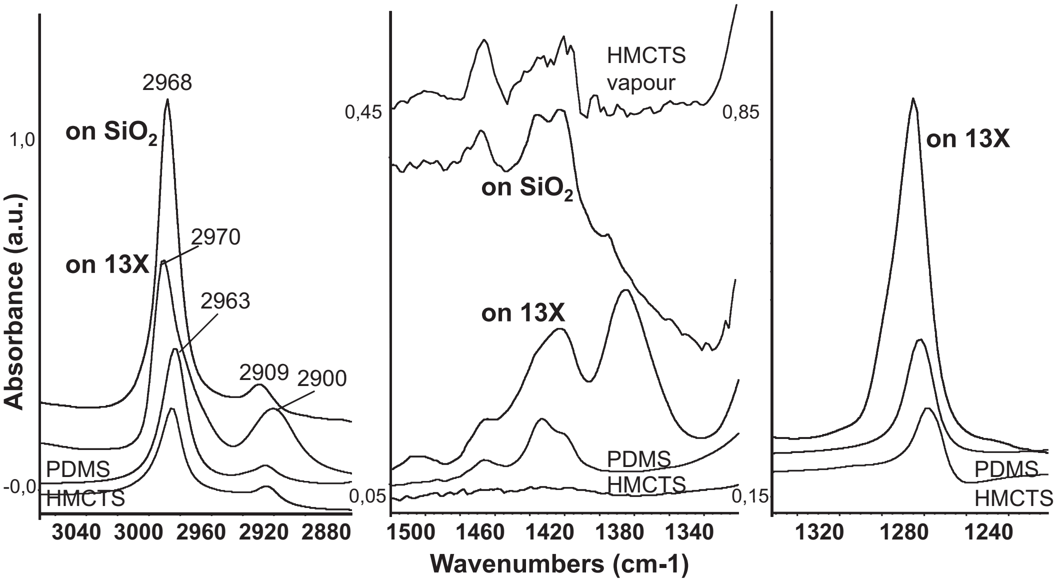

Fig. 6. Comparison of the IR spectra of HMCTS adsorbed on silica and on NaX zeolite with those of solid HMCTS (KBr disk), gaseous HMCTS and of polydimethylsiloxane film (PDMS).

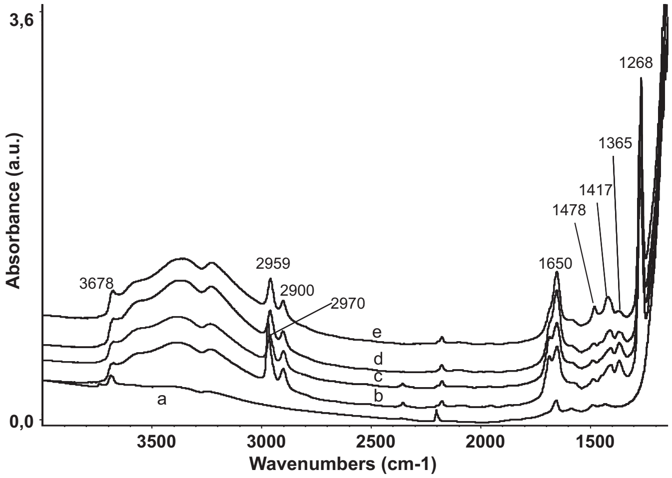

Fig. 7. FT-IR spectra od NaX zeolite after outgassing at 400 °C (a) after subsequent contact with HMCTS vapour (gas phase spectrum subtracted) (b), and following outgassing at r.t. 10 min (c), at r.t. 1 h (d), at 60 °C 10 min (e).

IR cell. Desorption is carried out by outgassing in vacuum upon heating.

3. Results and discussion

The adsorption capacities of the adsorbents, calculated as the amount of HMCTS adsorbed on the solid when the HMCTS vapour starts to be observed in the gas (i.e. after the time when its abatements is no longer complete), are reported in Table 1. These amounts, expressed as percent weight of adsorbed HMCTS per weight of adsorbent ($g_{\mathrm{HMCTS}}/g_{\mathrm{ADS}}$) are reported for one of the most efficient activated carbon [12], silica gel and X zeolite (Na-faujasite). It is clear that the effective adsorption capacity per unit weight of the activated carbon is higher than those of silica and faujasite, even taking into account the significantly higher apparent density of such inorganic materials (thus also per unit volume).

In Figs. 1 and 2 the spectra of spent NaX zeolite and silica gel, respectively, recorded after room temperature adsorption experiments, are compared with the spectra of the fresh adsorbents. In both cases the difference spectrum [spent adsorbent spectrum] – [fresh adsorbent spectrum] is compared with spectra of HMCTS and of the corresponding silicone polymer, polydimethylsiloxane (PDMS), reported as reference spectra in the same figures. Spectroscopic features due to adsorbed HMCTS but also due to PDMS polymer are detected for spent zeolite as well as for spent silica gel. The same result was observed also with the AC adsorbent after the same experiment [12].

In Fig. 3 the trends of the intensities of the bands of gaseous HMCTS during the desorption experiments from the three adsorbents are reported. The solid beds have been in contact with the flow of HMCTS-containing biogas until they have been completely saturated. Before saturation, the absorbance of the diagnostic band for HMCTS dropped to zero, while, after saturation, the absorbance observed for the untreated biogas was progressively recovered. The corresponding HMCT siloxane adsorption curves are reported in Fig. 4 for silica and zeolite materials while siloxane complete adsorption curve over active carbon is reported in ref. [12].

Curves reported in Fig. 3 have been recorded after switching the nitrogen purging flow on the column. We can see that, for the three adsorbents, the shapes of the desorption curve during purging with nitrogen at room temperature are almost identical, being essentially due to the slow evolution of HMCTS already present in the line after the adsorbent bed at the moment of the switch, and/or adsorbed on the walls of the line and of the IR cell. In fact, experiments performed with the empty reactor show that the diffusion of HMCTS vapour is much slower than those of methane and carbon dioxide. However, while HMCTS does not desorb from the NaX zeolite bed at 100 °C and 200 °C, it certainly desorbs from both AC and silica beds at these temperatures. In Table 1 the percent amount of HMCTS flowed out of the columns, with respect to HMCTS adsorbed in the beds, are reported for the desorption steps at 100 °C and 200 °C. The desorbed amounts have been calculated from the areas subtended on the IR absorption curves of the sensitive siloxane band upon purging with nitrogen. Indeed, the amount of siloxane desorbed from activated carbon is small, in agreement with the results of Boulinguiez and LeCloirec [15] that reported no desorption of siloxanes from activated carbons at temperature lower than 350 °C. Still incomplete desorption is found from the silica gel bed at 100 °C and 200 °C, although the amount of released siloxane is higher than in the previous case.

In Fig. 5 the spectra of silica before and after contact with HMCTS vapour are reported. The contact with HMCTS at room temperature (Fig. 5,b) causes the perturbation of the sharp band of isolated free surface hydroxy groups of silica from the typical value of 3747 cm^{-1} to near 3400 cm^{-1}, which is the central position of the broad band formed by the H-bonding interaction of the silanol groups with HMCTS. H-bonded silanol clusters, responsible for the broader absorption 3706– 3690 cm^{-1}, do not appear to be involved in such an interaction.

The spectrum of HMCTS is not perturbed very much upon adsorption, as apparent from Fig. 6 where its subtraction spectrum (i.e. the spectrum of the adsorbed species obtained by subtracting the spectrum of silica from the spectrum of HMCTS over silica) is compared with those of solid and gaseous HMCTS and of the polymer PDMS. The sharp CH_3 asymmetric stretching mode is shifted up to 2968 cm^{-1} from 2963 cm^{-1}, as observed on both solid HMCTS and polymer PDMS spectra. The corresponding CH_3 deformation modes observed in the region 1380–1460 cm^{-1} fall at frequencies close to those observed in the spectrum of PDMS, although their relative intensities are modified slightly. The bands in this region are not observed in the spectrum of solid HMCTS but can be detected at the same frequency in the spectrum of gaseous HMCTS.

In Fig. 5 the spectra of silica gel after contact with HMCTS vapour and following outgassing at room temperature and increasing time and at higher temperatures are also reported. An almost complete and rapid desorption has been reached only following heating under vacuum up to 150 °C. However, residual CH stretching modes are still detected (main band at 2968 cm^{-1}) at 200 °C, pointing out that HMCTS is still present as such or in some reacted form. Desorption of HMCTS results in the uncomplete restoring of surface hydroxyl groups band.

High temperature adsorption experiments have also been performed, looking at the evolution of gaseous species upon silica/HMCTS interaction (spectra in Figure S1, Supplementary Data). We do not observe formation of new gaseous species until 400 °C. At this temperature, gaseous methane forms, suggesting that deep conversion of HMCTS to silica occurs only at such temperature. Below this temperature ring opening polymerization to polydimethylsiloxane can occur without evolution of methane. In parallel, the band of free surface hydroxyl groups (3747 cm^{-1}) disappeared irreversibly, only leaving a broad absorption due to H-bonded OH's.

Analogous experiments have been performed on NaX zeolite (Fig. 7). Also in this case the molecular adsorption of HMCTS is observed (see bands in the CH stretching and deformation regions). However, a detailed analysis of the spectra show a vibrational perturbation, with a shift of the CH stretching bands and the formation of a new band at 1360 cm^{-1}, in the CH_3 deformation region (Fig. 6). We can remark that absorption in this region is present in the spectra of other siloxanes, linear and cyclic [16]. On the other side, the band at 1268 cm^{-1} (Si–CH_3 deformation mode) is slightly shifted towards higher frequencies with respect to the corresponding vibrational mode in pure HMTCS (1258 cm^{-1} in the solid HMTCS spectrum) and also in PDMS. This shift can indicate the presence of Si–R groups tightly held at the adsorbent surface, possibly CH_3–Si–O fragments [9]. Prolonged outgassing and heating at 60 °C already leads to significant modification of the spectra, i.e. changes in relative intensities of the deformation bands and the growth of a new component at 1478 cm^{-1}, indicating the occurrence of some surface complex reactivity. These data confirm that an even stronger adsorption occurs on NaX zeolite, than on silica and on ACs, possibly resulting in the ring opening. This agrees with the limited desorption of HMCTS, if any, from NaX.

4. Conclusions

The data reported here allow us to confirm our own and literature data showing that active carbons (ACs) are the choice material as adsorbent for HMCTS to purify biogases. Our experiments have been performed with a concentration of HMCTS far higher (250 times higher) than real one in landfill biogases, to allow one-day runs. In fact, we ascertained that the siloxane apparent adsorption capacity in the industrial plant is far lower than that measured in the lab experiments, likely due to the copresence of many other impurities in the real biogas. On the other hand, we suppose the data allow to rank different adsorbents with respect to their adsorption capacity for siloxanes. Desorption experiments with on-field exhausted ACs, some of which have been reported previously [12], appear to be quite consistent with those concerning samples used in the lab.

According to these data, inorganic materials, i.e. silica and NaX zeolite, present very limited or no advantages. In fact they are not only less efficient (on both weight and volume bases) than pure ACs in the adsorption step, but show similar difficulties also in the regeneration step. In our adsorption tests (synthetic biogas enriched with HMCTS) on silica and NaX zeolite, polymerization of HMCTS to silicone is proposed to occur already at room temperature during the adsorption step, resulting in adsorbent deactivation as previously found for ACs. Only a fraction of adsorbed HMCTS can be recovered from silica and, even less, from active carbon by purging with nitrogen at 20 to 200 °C. On NaX zeolite, purging at room temperature allows some HMCTS be recovered, if any, while no further desorption could be detected at increasing temperature. On silica, the adsorption of HMCTS occurs by hydrogen bonding on the surface silanol groups, which are only partially freed by outgassing up to 200 °C. At even higher temperatures HMCTS converts to silica releasing methane. Adsorption on NaX zeolite is not only molecular, producing also new species whose identification is now under study.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2010.10.032.

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