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Adsorption Equilibrium of Light Mercaptans on Faujasites

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Abstract. Both thermogravimetry and manometry coupled to calorimetry techniques were used to determine the adsorption equilibrium of ethyl mercaptan in pure and extruded NaX zeolites. Sorption isotherms were investigated from 298 to 373 K, and over a large range of pressure from 10^{-4} to 100 hPa. Adsorption heats were measured at 298 K. Reversible adsorption-desorption isotherms are type I shaped and characterize a very high adsorption affinity of NaX zeolites for ethyl mercaptan. The sulfur compound entirely probes NaX zeolite α-cages at micropore saturation. The presence of the mineral binder for the extruded zeolite does not affect the adsorption phenomenon. Adsorption data were well fitted using the Polanyi-Dubinin model. Calorimetric and isosteric heats do not change very much with loading, indicating that NaX zeolite is energetically homogeneous for the adsorption of ethyl mercaptan. Additional information concerning state of adsorbed phase were obtained from isosteric molar entropy curves. Therefore, the NaX faujasite appeared as a powerful potential candidate for industrial desulfurization of natural gas by adsorption process.

Keywords: adsorption, zeolite, ethyl mercaptan, thermogravimetry, calorimetry

1. Introduction

Traditional processes for natural gas treatment do not enable to reduce sulfur contents down to very low concentrations. Although traditional processes are still being improved, development of new processes using adsorption phenomena are now in progress, in order to lower specific sulfur compounds, more precisely mercaptans, down to very low concentration, required by future environmental legislation.

Published data concerning the removal of light mercaptans by adsorption process are scarce (Sakano et al., 1999; Changsub et al., 2001; Bashkova et al., 2002). Activated carbons either as they are or modified by some reagents have been mainly used as sulfur compound adsorbents in environmental engineering (Chiang et al., 2000; Bagreev et al., 2000; Changsub et al., 2001). It has been reported that methyl mercaptan is converted to dimethyl disulfide on the surface of activated carbons. The presence of different functional groups on the surface and metal ions can moreover enhance the oxidation of methyl mercaptan (Dalai et al., 1997). Some studies have also shown the importance of water in the oxidation process (Bagreev et al., 2000, 2002). It has also been demonstrated that activated carbons impregnated with various chemicals work well as methyl mercaptan adsorbents (Turk et al., 1989; Sakano et al., 1997; Chiang et al., 2000). The literature

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survey clearly indicates that the performance of activated carbons greatly depends on the surface characteristics and the porous texture of the material (Bashkova et al., 2002). However, although its adsorption characteristics are attractive, activated carbon is difficult to regenerate because of its combustibility and the presence of solid sulfur compounds when modified by some reagents. Therefore, the use of zeolites instead of activated carbons as light mercaptan adsorbent may be another interesting alternative to be explored, all the more so because only a very few studies are published. For example, one paper reports on adsorption and surface chemistry of ethyl mercaptan and n-butyl mercaptan on MFI zeolites (Garcia et al., 1991). Another investigates adsorption properties of A-type zeolites to remove pungent smell components from a coffee aroma-containing gas (Sakano et al., 1996). Sarbak (1996, 2001) has tested ion-exchanged X and Y faujasites for the desulfurization of ethyl mercaptan and the elimination of odors produced as by-product in the pharmaceutical industry and food processing plants. Recently Wakita (2003) describes a method for removing dimethylsulfide and/or tertiary butyl mercaptan present in the city gas by using an adsorbent containing one of faujasite, β, L and MFI type zeolite. This patent provides a method for removing the sulfur compounds in which the adsorbent is intermittently regenerated.

In this study, the adsorption of pure ethyl mercaptan in two NaX zeolite samples was investigated using both a gravimetric balance and calorimetry. The aim of this work was to obtain equilibrium thermodynamic data to characterize the evolution of the system under study and more specifically in the range of very low pressure and thereby, to test the feasibility of using NaX zeolites in an industrial process for natural gas desulfurization by adsorption.

2. Material and Methods

Two NaX zeolites were used in this study. The former distributed by Union Carbide was a pure powdered sample and contains crystals of nearly uniform size (1 μm). The chemical formula of the anhydrous zeolite was $Na_{86}(AlO_2)_{86}(SiO_2)_{106}$. The other faujasite in the form of spherical pellets (0.6 mm) was produced by CECA. The company for sake of confidentiality did not divulge the nature and the amount of the pellet binder.

Ethyl mercaptan, which has a purity of 97%, was supplied by Sigma-Aldrich. Before use, the chemical was degassed under high vacuum then stored in an evacuated vessel containing a 3A hydrophilic zeolite to adsorb any residual water.

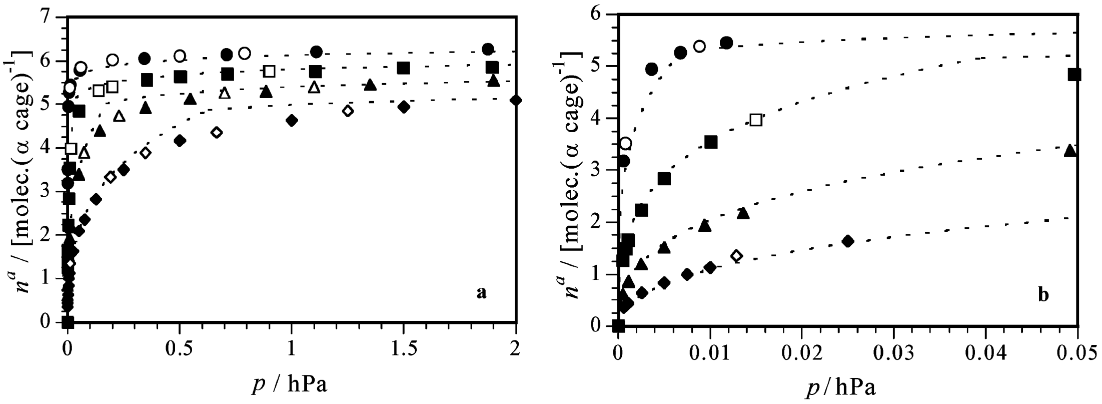
A gravimetric balance (McBain) was used to measure the isotherms of ethyl mercaptan in around 25 mg of zeolite, which has been outgassed under a vacuum of 10^{-5} hPa at 673 K for more than 12 h prior to the sorption measurements. The sorption isotherms were investigated at 298, 323, 348 and 373 K. The isotherm temperature was controlled by an Eurotherm temperature controller. The sorption isotherms were measured in dynamic mode by increasing (for adsorption) or decreasing (for desorption) the equilibrium pressure in small increments. The method consisted in introducing the gaseous adsorptive at a very low flow rate into the balance by means of a microvalve and then controlling under high vacuum the pressure by a VAT throttling valve and adaptive pressure controller connected to a MKS pressure sensor. This method permits to control vapor pressures in the range from 5 10^{-5} hPa to 10 hPa for several days with a high accuracy (for example $\pm$ 0.1 10^{-5} hPa at 5 10^{-5} hPa).

A differential heat flow Setaram C80 calorimeter coupled to a conventional manometric apparatus was used to measure adsorption heats of ethyl mercaptan on NaX zeolites. The experimental device was implanted as in the case of gravimetry in a well-ventilated environment for sake of security. The amounts of ethyl mercaptan adsorbed at increasing constant pressure and at constant volume, were calculated from a mass balance of the gaseous phase before and after each adsorption experiment, considering ethyl mercaptan was an ideal gas. In regards to the operating conditions, measured adsorption heats were similar to the differential molar adsorption enthalpies and isosteric heats. Experiments were performed at 298 K in a pressure range from 10^{-4} hPa to 100 hPa, on ca 500 mg of zeolite activated under vacuum at 673 K for a night.

3. Results and Discussion

3.1. Sorption Uptake

The adsorption-desorption isotherms at 298, 323, 348 and 373 K of ethyl mercaptan on the free binder NaX zeolite are shown in Figs. 1(a) and (b). They are reversible and do not display any hysteresis upon desorption of mercaptan. The adsorption process does not induce any catalytic decomposition of the adsorbate. These isotherms are of type I according to the IUPAC classification (Sing et al., 1985) and are typical



(a) (b)

Figure 1. Adsorption (close symbols) and desorption (open symbols) isotherms of ethyl mercaptan in pure NaX at temperatures of (from top to bottom) 298, 323, 348 and 373 K over the pressure ranges 0–2 hPa (a) and 0–0.05 hPa (b). Dashed lines are the fits of the Dubinin-Radushkevich model. Symbols are experimental data obtained by thermogravimetry.

for microporous adsorbents. They are steep at the beginning of the adsorption process, indicating a high adsorption affinity of ethyl mercaptan for NaX zeolite. However, the Henry law was not observed although adsorption measurements were performed at very low pressures from 10^{-5} hPa. Above a pressure of around 0.2 hPa the isotherm at 298 K displays a plateau region indicative of the filling-up of micropores (Figs. 1 and 2). The volume of mercaptan adsorbed at this plateau, calculated by assuming the density of the adsorbed phase is that of the liquid at 298 K, is very close to the geometric volume of α-cages (0.294 $cm^3.g^{-1}$) of the NaX zeolite (Fig. 2). By comparison and assuming too that the density of the adsorbed phase is that of the liquid at higher temperatures, the amount adsorbed at around 1.9 hPa (far below micropore saturation) is 0.265, 0.259 and 0.244 $cm^3.g^{-1}$ at 323, 348 and 373 K, respectively.

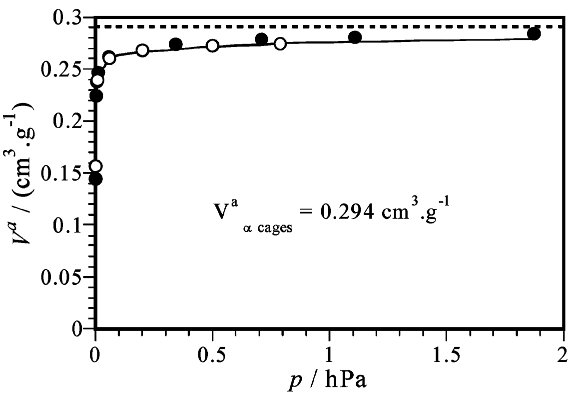


Figure 2. Adsorption (close symbols) and desorption (open symbols) isotherm of ethyl mercaptan in pure NaX zeolite at 298 K, obtained by thermogravimetry. Dashed line is the geometrical volume of α-cages of NaX zeolite.

As anticipated, ethyl mercaptan molecules are too large to be adsorbed within β-cages and only probe α-supercages. By this, it is implied that the volume of α-cages defines the maximal adsorption capacity of the NaX zeolite for ethyl mercaptan.

Adsorption data were further analyzed using the classical models of Langmuir and Polanyi-Dubinin. The Langmuir model did not reproduce the high amount of mercaptan adsorbed at low pressure. Indeed, it assumes an ideal gas model where molecules are bound to adsorption sites with identical energy and neglects interactions between the adsorbent and molecules.

In return, the Polanyi-Dubinin model matches very well the sorption isotherms obtained in the temperature range between 298 and 373 K and all over, the explored pressure range (Figs. 1(a) and (b)). Adsorption data were fitted to the Dubinin-Radushkevich (DR) equation (Dubinin et al., 1947) expressed as follows:

$$\log V^a = \log W_0 - 2.3(R/E)^2[T \log(p_s/p)]^2 \quad (1)$$

where V^a is the volume of liquid-like ethyl mercaptan adsorbed per unit mass at the pressure p, W_0 is the maximal micropore volume accessible to the adsorbate, p_s is the saturated vapor pressure at the temperature T of the sorption isotherm, E is a characteristic adsorption energy. The characteristic curve shown in Fig. 3 highlights two distinct adsorption

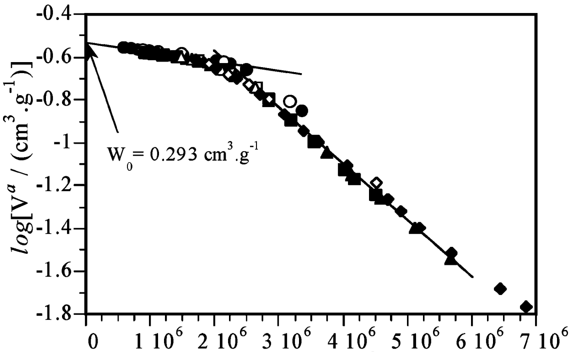


Figure 3. Characteristic curve of the Dubinin-Radushkevich model applied to adsorption data of ethyl mercaptan in pure NaX at 298 (circle symbols), 323 (square symbols), 348 (triangle symbols) and 373 K (lozenge symbols). W_0 is the maximal micropore volume accessible to the adsorbate.

domains. The one observed up to a micropore loading of 0.234 $cm^3.g^{-1}$ (5.3 molec.α-cage^{-1}) characterizes molar adsorption energy typical of adsorbent/adsorbate interactions of 24.5 $kJ.mol^{-1}$. At higher loading, the second domain defines a microporous volume (W_0) of 0.293 $cm^3.g^{-1}$ (6.6 molec.α-cage^{-1}) very close to the geometric volume of the NaX α-cages and stronger adsorption energy of 60.2 $kJ.mol^{-1}$. Normally, the initial domain should have a higher energy, and consequently a smaller slope than the upper domain. This behavior which was observed too for the adsorption of other organic compounds on MFI zeolites (Garrot et al., 2002) appears to be in contradiction with the results we would expect.

Sorption isotherms on spherical pellets of NaX zeolite were further drawn for comparison to investigate the behavior of the binder during the adsorption process. Sorption isotherms obtained on the pellets are similar in shape to those obtained on the pure powder. At constant temperature and pressure, the adsorption capacity expressed in amount adsorbed per unit mass of activated sample is nevertheless lower for the extruded sample than for the pure material, because of the presence of the binder. A percentage of binder of 12.8 % was estimated from the ratio between the adsorption capacity of the pure NaX zeolite and that of the extruded zeolite. A very good agreement between adsorption data obtained on the pure zeolite and those majored by 12.8% for the extruded zeolite was observed (Figs. 4(a) and (b)), indicating that the binder does not modify adsorption properties of the NaX zeolite for ethyl mercaptan. Therefore, the isotherms on the pellets of NaX zeolite were well described by the Dubinin model and the characteristic values of the uptake at the intersection of the two filling domains and the micropore volume were 12.8% lower than those obtained for the pure zeolite.

3.2. *Adsorption Heat*

Adsorption heats of ethyl mercaptan on NaX were characterized in two ways: (i) by experimental calorimetric values (Q^a_{cal}) and (ii) by calculated isosteric values (Q^a_{iso}).

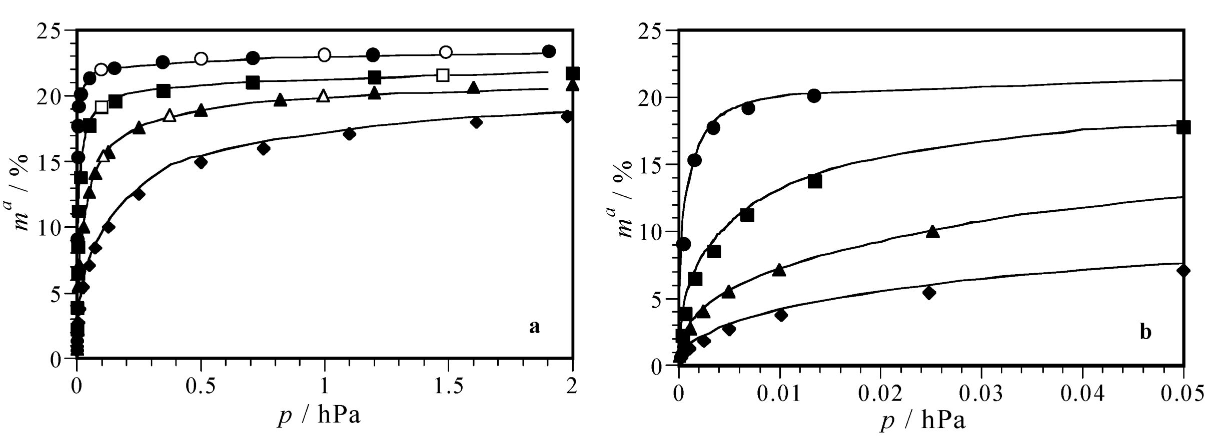


Figure 4. Adsorption (close symbols) and desorption (open symbols) isotherms of ethyl mercaptan in pellets of NaX at temperatures of (from top to bottom) 298, 323, 348 and 373 K over the pressure ranges 0–2 hPa (a) and 0–0.05 hPa (b). Symbols are experimental thermogravimetric data recalculated considering that the amount of binder in the zeolite was 12.8 %. Solid lines are the corresponding isotherms obtained on pure NaX.

Isosteric heats were calculated indirectly from the set of isotherms obtained on the NaX zeolite by drawing the corresponding isosteres in the following representation, at various loadings:

$$\ln(p/p^0) = [f(1/T)]_m \tag{2}$$

knowing that:

$$Q^{\mathrm{a}}_{\mathrm{iso}} = RT^2[\partial \ln(p/p^0)/\partial T]_m \tag{3}$$

where p^0 is the standard pressure.

The dependence on loading of the isosteric and calorimetric heats of adsorption of ethyl mercaptan in binder free NaX zeolite is shown in Fig. 5. A very good agreement between calculated and measured values was observed. Heat curves obtained on the extruded zeolite showed the same shape. The presence of binder does not modify significantly heats of adsorption.

Figure 5 shows that heat of adsorption of ethyl mercaptan in NaX zeolite increases slowly with loading at 298 K. This behavior indicates that either molecules are adsorbed on isoenergetic sites or the decrease of adsorbent/adsorbate interactions with loading is counterbalanced by the increase of adsorbate/adsorbate interactions. Globally, the heat of adsorption increases from 65 kJ.mol^{-1} at zero loading up to 75 kJ.mol^{-1} at high micropore loading because of increasing adsorbate/adsorbate interactions, before decreasing down to the heat of vaporization of ethyl mercaptan at micropore saturation. The initial net heat of adsorption of ethyl mercaptan (37.5 kJ.mol^{-1}) defined by the difference between the heat of adsorption and the heat of vaporization, is slightly lower than that of methanol (39.8 kJ.mol^{-1}) reported in the literature (Kiselev, 1969). These data highlight the smaller interaction of ethyl mercaptan molecule with the zeolite micropore network due to lower dipole moment. For comparison the initial net heat of adsorption of the non-polar ethane molecule (16.1 kJ.mol^{-1}) is more than two times lower than that of ethyl mercaptan. A steep increase in the heat of adsorption of more than 15 kJ.mol^{-1} was in addition observed in a very narrow range of micropore loading on approaching saturation. A possible explanation for this strong reproducible exothermic effect is that the confinement of mercaptan molecules within α-cages of the zeolite induces very strong adsorbate/adsorbate interactions at high loading.

3.3. Molar Entropy of the Adsorbed Phase

To go further in the thermodynamic characterization of the adsorption process, isosteric molar entropies [$\Delta_{\mathrm{ads}}S_{\mathrm{m}}$ (m)] were determined as a function of loading up to around 0.20 g.g^{-1} (5.4 molec.α-cage^{-1}), from the set of isosteres previously defined in Section 3.2. The molar entropy of the adsorbed phase [$S_{\mathrm{m}}(m)$] at constant loading was thereafter calculated by the following relation:

$$S_m(m) = \Delta_{\mathrm{ads}}S_m(m) + S^0_m(g) \tag{4}$$

where S^0_{m} (g) is the absolute molar entropy of the gas at 298 K. Molar entropies of ethyl mercaptan were also evaluated considering the calorimetric heat curve and

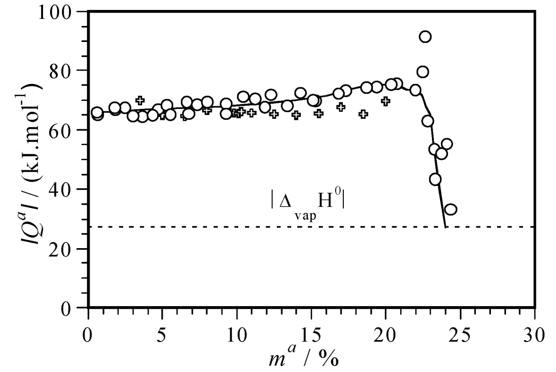


Figure 5. Calorimetric (circle symbols) and isosteric (cross symbols) heats of adsorption of ethyl mercaptan in pure NaX zeolite as a function of loading, at 298 K. Dashed line is the heat of vaporization of ethyl mercaptan.

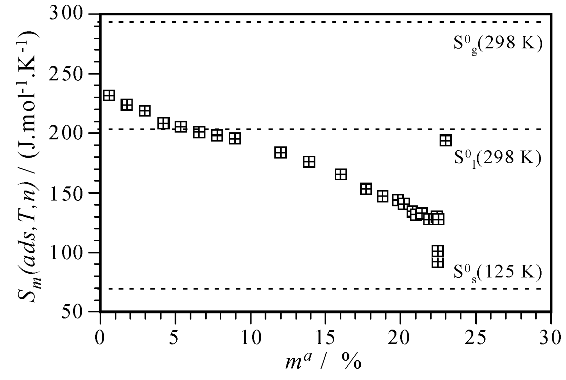


Figure 6. Dependence of molar entropy of ethyl mercaptan adsorbed in pure NaX, on loading. Dashed lines from top to bottom are the absolute molar entropies of the gas and the liquid at 298 K and that of the solid at 125 K.

the sorption isotherm at 298 K to explore the filling domain close to micropore saturation.

Figure 6 shows the dependence of the molar entropy of the adsorbed phase on loading. As soon as the first amount of ethyl mercaptan is adsorbed, the adsorbed phase behaves like a compressed gas. On increasing loading, it is like a liquid phase at around 0.07 $g.g^{-1}$ (2 molec.α-$cage^{-1}$) then comes close to a solid phase on approaching micropore saturation.

4. Conclusion

This thermodynamic study contributes for the first time to the knowledge of the evolution of the systems zeolite/mercaptan under equilibrium conditions, and more specifically in the range of low pressures. NaX faujasites show a very high adsorption affinity for ethyl mercaptan and its maximal adsorption capacity is that of α-cages. The presence of a binder for the extruded zeolite does not modified the adsorption process. By this, it follows that the NaX zeolite appears as a powerful microporous adsorbent to trap pure gaseous ethyl mercaptan traces and therefore, it may be used in an industrial process for natural gas desulfurization by adsorption.

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