

ZEOLITES AS ADSORBENTS OF ATMOSPHERIC AND WATER POLLUTANTS

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ABSTRACT

In this study, adsorption of atmospheric and water pollutants on chosen zeolites has been studied. N₂O and CO have been adsorbed from the gas phase on ZSM-5 and MOR zeolites. The adsorption of water pollutants: phenol, nicotine and pharmaceutically active compounds (salicylic acid, acetylsalicylic acid and atenolol) have been probed on ZMS-5, β and clinoptilolite. The adsorbents have been used as synthesized or after modification procedures. The adsorption was studied at 303 K, by titration microcalorimetry, employed to obtain the heats evolved as a result of adsorption either from the gas or liquid phase. Adsorption experiments were performed under the same conditions. The maximal adsorption capacities of investigated solids against specific pollutants have been determined; the effect of zeolite' modification have been considered, too. The obtained results show that zeolites can be used effectively in the removal of investigated atmospheric or water pollutants.

Keywords: adsorption, phenol, nicotine, pharmaceutically active compounds, zeolites.

INTRODUCTION

Zeolites are three-dimensionally ordered solids, composed of basic tetrahedral TO₄ units (T-atoms usually refer to Si or Al) that can form so-called secondary building units of different types of cylinders or cages. The unique features expressed by these materials originate from the fact that these cylinders or cages form a network of pores in the crystal; these pores being accessible from the outside. Zeolites also possess unique stability; all these characteristics make these materials interesting for many different applications: besides the others, the separation processes and also the adsorption on the outer or inner surface [1].

The pollution of the environment is very complex problem: numerous chemicals recognized as poisonous or dangerous in any other sense come in the environment mainly as a result of anthropogenic actions. Atmosphere [2,3], waters and soils [4,5] may contain different organic and inorganic residues present in a wide range of concentrations. This work presents results related to the applicability of chosen zeolite types (MOR, MFI, BEA, HEU) as adsorbents for some atmospheric (N₂O, CO) or water (phenol, nicotine, pharmaceuticals) pollutants.

EXPERIMENTAL

The adsorption of N₂O and CO on ZSM-5 zeolite (Si/Al = 50, home made and modified by presence of different charge-balancing cations) and on MOR zeolite (Norton) have been studied by means of microcalorimetry. A system composed of heat-flow microcalorimeter of the Tian-Calvet type (C80 Setaram) linked to a glass volumetric line enabled the introduction of successive known doses of adsorbed gas and the determination of differential heats of adsorption as well as the adsorption isotherms. Before the adsorption, the samples were pre-treated in vacuum (10⁻³ Pa) overnight, at 673 K.

The adsorption of water pollutants has been studied by titration microcalorimetry (Titrys from Setaram). The samples were pre-treated under vacuum at 423K for 2 h before being transferred into the calorimeter. Using a syringe pump, successive pulse injections of known amounts of a solution were sent onto the sample maintained at 303K at 2 h time intervals cell. Adsorption experiments were performed under the same conditions, the equilibrium adsorbate concentrations were determined by fluorescence spectrophotometer (PTI 1609 from Photon Technology International). Here, the possibilities to adsorb aqueous solution of phenol (0.03 mol/L, Sigma–Aldrich, 99+%), nicotine (0.03 mol/L, (Sigma–Aldrich, 99+%) salicylic acid, acetylsalicylic acid and atenolol (purchased from pharmaceutical company “Galenika”, Belgrade, Serbia, concentrations of solution between 2 and 3 mmol/L) have been estimated. Nicotine and phenol were adsorbed on zeolite BEA (β , Si/Al = 12.5 and 43, “Rhone-Poulenc”), MFI (ZSM-5, Si/Al = 15, 40 and 140, “Zeolyst”; the modifications have been done by ion-exchange from aqueous solutions of specific cations, monometallic or bimetallic forms were obtained) and HEU (natural clinoptilolite, “Zlatokop” Serbia, Si/Al = 5); and, for the sake of comparison, on one activated carbon (Aldrich, $S_{\text{BET}} = 1600 \text{ m}^2/\text{g}$). Pharmaceuticals were adsorbed on clinoptilolite modified with cations sorbed from aqueous solutions: Cu(II), Zn(II), Ni(II) or Mn(II) (2.9 % wt., 1.5% wt., 1% wt., and 0.9 % wt., respectively).

The crystallinities of adsorbents were checked by X-ray diffraction, before and after adsorption, using Bruker (Siemens) D5005 diffractometer at room temperature using Cu $K\alpha$ (radiation, 0.154 nm) from 3° to 80° 2 θ in a 0.02°steps with 1 s. The possibility to perform the regeneration of adsorbents was investigated by thermal desorption (temperature programmed desorption – TPD). These measurements were performed on a thermo-balance coupled with differential scanning calorimeter (TG–DSC 111 from Setaram), capillary-coupled by a mass spectrometer (MS, Thermostar from Pfeifer) as a detector. The TPD experiments were carried out in a flow, with helium as the carrier gas (20 ml min⁻¹).

RESULTS AND DISCUSSION

As it has been determined previously by means of infrared spectroscopy, the active sites for adsorption of N₂O and CO are charge-balancing cations [6] In our work, it has been shown that the amount of adsorbed pollutants depend on the type and the amount of charge-balancing-cation. Table 1 presents quantitative data on the adsorption of N₂O and CO found in this work. Besides, the heats of adsorption have shown the differences in the affinities of different samples against both gases [7-8]. Importantly, higher differential heats found for the adsorptions of CO have shown that in the case of co-adsorption form the gas-mixtures, CO should be preferably adsorbed.

Table 1. Quantitative data on the adsorption of N₂O and CO on the investigated samples.

Sample	Irreversibly adsorbed N ₂ O ($\mu\text{mol/g}$)	Irreversibly adsorbed CO ($\mu\text{mol/g}$)
CuZSM-5	40.0	110
FeZSM-5	5.5	7.1
CoZSM-5	5.0	4.5
Cu,FeZSM-5	15.0	120.0
Fe,CuZSM-5	5.5	53.0
Cu,CoZSM-5	17.0	60.0

The adsorption capacities against specific water pollutants depend on the structure of solid material and on the characteristic of pollutant’s molecule. Figure 1 (left) presents adsorption isotherms of nicotine, while Figure 1 (right) shows adsorption isotherms of phenol

obtained on different adsorbents. Figure 2 (left) shows the profiles of differential heats revealed as a function of the amounts of nicotine adsorbed on zeolite β (with different Si/Al ratio) and activated carbon, which is used as a reference material known to be active in adsorption of many water pollutants [9]. The values and the profiles of differential heats clearly show that zeolite β has adsorption capacities that are comparable with that on of activated carbon ($S_{\text{BET}} = 1600 \text{ m}^2/\text{g}$). It has been found that the adsorption possibilities of ZSM-5 zeolites are significantly lower. Similar stands for the adsorption of phenol from aqueous solutions (not presented here) [10].

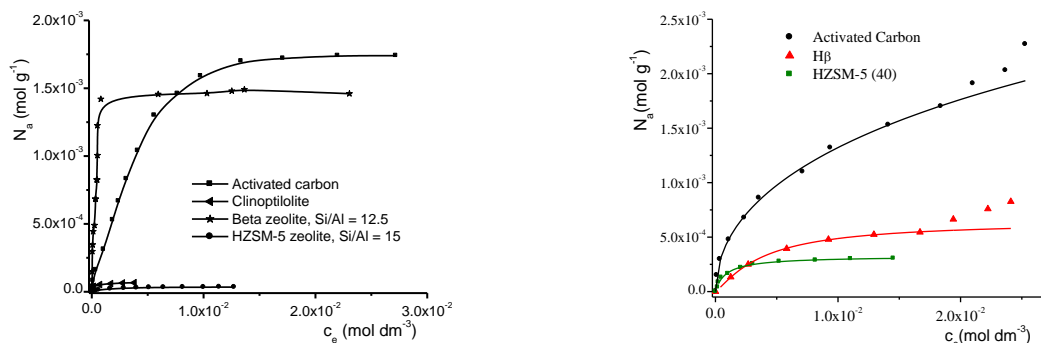


Figure 1. The adsorption of nicotine (left) and of phenol (right) from aqueous solution onto the activated carbon and various zeolites.

On Figure 2 (right) the profiles obtained for the adsorption of one β -blocker, atenolol on natural clinoptilolite, are shown. Modified clinoptilolites have shown higher capacities in comparison with natural mineral; the adsorption capacities are dependent on the type of metallic cation present in the structure. Similar behaviour was obtained for the adsorption of salicylic and acetylsalicylic acids. The maximal adsorption capacities of investigated natural zeolite (clinoptilolite) toward chosen pharmaceuticals lie in the range of $10^{-5} - 10^{-6} \text{ mol/g}$.

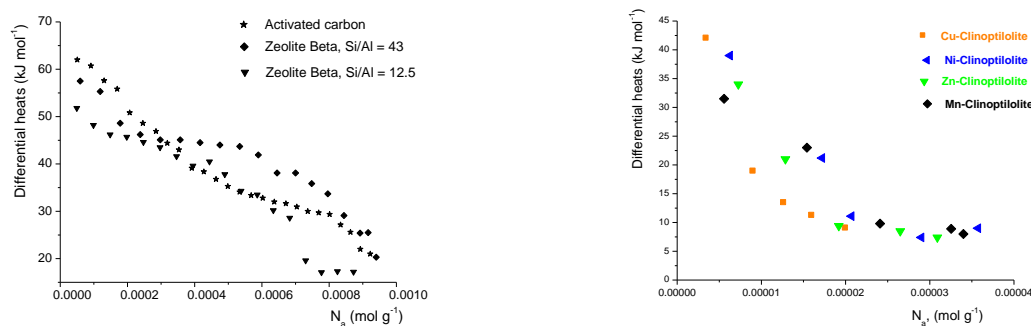


Figure 2. The profiles of differential heats of adsorption obtained (left) for nicotine on zeolite β and on activated carbon, and (right) the profiles of differential heats of atenolol (pharmaceutical, β -blocker) on modified clinoptilolite, purchased from “Zlatokop”, Serbia.

In our work, the possibilities of regeneration of used solid samples applied for pollutants adsorption from aqueous solution have been tested. As explained in Experimental section; pollutants have been desorbed from the solids using thermal desorption method. Figure 3 shows a case of ZSM-5 regeneration after nicotine or phenol adsorption. The profiles of mass loss and TPD profiles of water and pollutants’ desorption are presented.

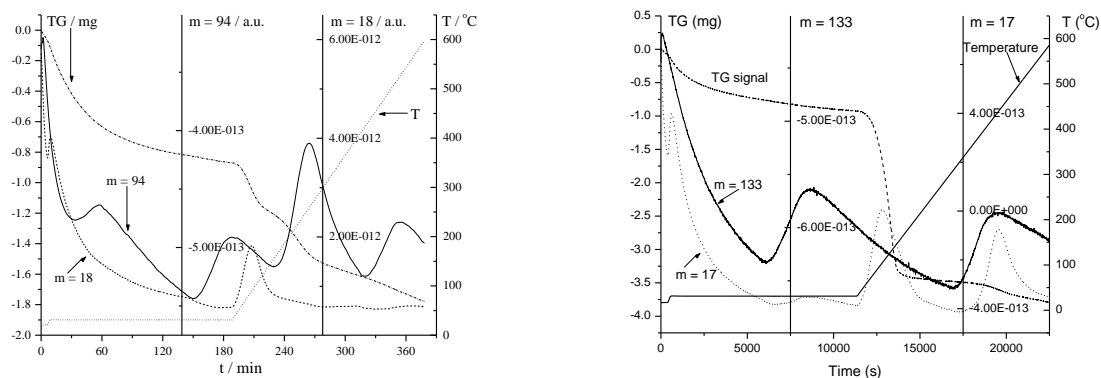


Figure 3. The regeneration of ZSM-5 (Si/Al = 15) after the adsorption of phenol (left) and nicotine (right). Figure presents the results obtained during the temperature programmed heating of this sample: TG signal and TPD profiles of water ($m/e = 18$ and 17), phenol ($m/e = 94$) and nicotine ($m/e = 133$).

CONCLUSION

The results obtained in this work show that natural and synthetic zeolites can be used effectively in the removal of investigated pollutants from the gas or liquid phase. Their adsorption capacities can be adjusted using different modification procedures. Importantly, in the case of water pollutants, the maximal values of specific pollutants that can be adsorbed on investigated zeolite are higher than the concentrations found in the wastewaters, lake or rivers, nowadays. Generally, it has been shown that the used samples can be regenerated; the structures of all investigated zeolites remain un-changed after adsorption procedures.

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