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Nanosorbents for selective removal of odours

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Y type zeolites modified with Cu, Ni, Mn as well as mesoporous hexagonally ordered silicates and niobosilicates of MCM-41 type with gold dispersed as an active component were studied in odour adsorption. Dibutyl sulfide and butyl amine were used as odour components and they were adsorbed separately and in the presence of high moisture content. The attractiveness of Au/MCM-41 samples for the selective adsorption of both odour compounds (much higher for the sulfide) and their possible further oxidation during the recovery of sorbents has been proved. The highest resistance for moisture adsorption was found for Au/NbMCM-41.

Key words: *Y zeolites containing Cu, Ni, Mn; Au/MCM-41, Au/NbMCM-41; dibutyl sulfide; butyl amine*

1. Introduction

Recently, regulations concerning environmental protection have been concentrated on odour emissions. However, these regulations and guidelines to avoid odour annoyance presently differ from country to country [1]. It is because the so called "odour problems" are very complex issues. One point is a large variety of odour emission sources which can be divided into odours due to fermentation (i) and odours from processing plants (ii) [2]. Each of these categories includes a lot of sources which have not been systematically recorded, characterised, and evaluated so far. Talking about odour treatment technologies, one should define the source, taking into account whether the removal unit can be maintained on the way of odour emission (e.g., in power station or viscose industry) or it should be located in the area where odours are concentrated (e.g., agricultural origin, composting plants, food industry). Depending on that, various units and various technologies can be applied.

Another important task is chemical composition of odours and physical conditions for which a suitable treatment system should be selected. In order to do so, a detailed knowledge is needed about advantages and disadvantages of various technologies available for off-gas treatment. An overview of such technologies is presented in [1].

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Long term exposed odours are often removed by biological units. However, they are not sufficient for the reduction of malodours below the odour threshold. To reduce concentrations below odour threshold, selective adsorption processes with on-site regeneration of the adsorbents are very promising [3]. Looking for selective adsorbents, one should take into account the nature of odour compounds (most of them are organic compounds containing nitrogen and/or sulphur) and the nature of elements (located on the surface of sorbents) which are active for the selective adsorption. Our former study [4] indicated that nickel located on the surface of mesoporous molecular sieves of MCM-41 type is an attractive component for selective adsorption of sulfides and their further oxidation with hydrogen peroxide. In the patent literature [5], one can find the description of gold grafted on silica-alumina system used for the removal of malodour.

In this contribution high pore volume nanomaterials (zeolites and mesoporous MCM-41 materials) modified with active components (Ni, Cu, Mn, Au) have been fabricated to obtain sorbents able to concentrate a maximum amount of pollutants in a minimum volume of adsorbent. A choice of active components was determined by the expected selectivity to sulfides and/or amines and a possible further recovery of sorbent via the catalytic oxidation of odours at room temperature. Butyl amine ($BuNH_2$) and dibutyl sulfide (Bu_2S) were adsorbed on the prepared materials in the presence and in the absence of water vapour.

2. Experimental

Preparation and modification of mesoporous catalysts. Mesoporous molecular sieves of MCM-41 type have been synthesized by the hydrothermal method [6] and modified in the preparation of NbMCM-41 according to [7]. Au/MCM-41 and Au/NbMCM-41 catalysts were prepared by incipient wetness impregnation of the MCM-41 support with $HAuCl_4$ (Johnson Matthey) with loading of gold of 1 wt. %. The amount of solution used was chosen in such a way that the liquid filled up only the pores of the mesoporous support. Following the impregnation, the catalysts were dried at 373 K for 5 h and calcined at 773 K for 3 h in the air. After calcination, Au-modified MCM-41 materials were reduced in H_2 (5 vol. % H_2/N_2) at 773 K for 3 h.

Modification of zeolite catalysts. Cu-NaY, Mn-NaY and Ni-NaY catalysts were prepared from NaY zeolite (Si/Al = 2.6, Katalistiks) with copper(II) acetate (POCH, Poland), manganese(II) acetate (Aldrich) and nickel(II) nitrate (Aldrich) water solutions, respectively, by ion exchange at 323 K. The obtained samples, after filtration and washing, were calcined at 673 K for 4 h.

XRD patterns. The XRD patterns have been obtained on a TUR-62 diffractometer using CuK_α radiation ($\lambda = 0.154$ nm), with a step size of 0.02° and 0.05° in the small-angle and high-angle ranges, respectively.

N_2 adsorption/desorption. The surface area and pore volume of the samples were measured by nitrogen adsorption at 77 K, using the conventional procedure, with

a Micromeritics 2010 apparatus. Prior to the adsorption measurements, the samples were degassed in vacuum at 573 K for 2 h.

Adsorption of odours. Adsorption of odours – dibutyl sulfide (Bu_2S) and butyl amine ($BuNH_2$) in the presence and absence of water vapour as well as adsorption of water were performed in two manners, both at room temperature. In the former method, the outgased sorbents were weighed into vessels and put into the desiccator at the place with the highest odour concentration and kept for 7 days. After a certain storage time, the treatment efficiency of the considering medium was analysed by weight and chemical analysis. In another method, the outgased sorbent was put on the balance scale in a glass box purged with nitrogen flow. In this box, an appropriate odour was evaporated and the amount of adsorbed compounds was continuously weighed, the course of the weight change was recorded by a computer program and adsorption isotherms were plotted.

3. Results and discussion

Among commonly used adsorbents, zeolites, exhibiting the crystalline structure and uniform, well defined pores, seemed to be attractive for the study. We have used an Y type zeolite of high sorption capacity (ca. 25 vol. %) modified with transition metals (Ni, Mn, Cu) to obtain high selectivity in the chemisorption of odours.

Another, relatively new, nanosorbents applied in this work, were mesostructured materials of MCM-41 type modified with niobium and gold. They are attractive because of very high surface areas (often exceeding 1000 m^2/g) and pore volumes ca. 0.7 cm^3/g. Moreover, the uniform hexagonally ordered mesopored tubes make the diffusion of sorbats in pores easy. The silicate and niobosilicate materials were modified with gold to obtain high selectivity in sulfide and amine sorption. The texture/structure parameters of these sorbents are given in Table 1. One can notice very high surface areas (ca. 1000 m^2/g) and pore volumes (ca. 1 cm^3/g).

Table 1. Characteristic of the mesoporous catalysts

Catalyst	Surface area $[m^2 \cdot g^{-1}]$	Pore volume $[cm^3 \cdot g^{-1}]$	Pore diameter [nm]
SiMCM-41	1075	1.25	3.90
NbMCM-41	955	1.12	3.84
Au/MCM-41	1056	1.12	3.82
Au/NbMCM-41	901	0.99	3.62

The nitrogen adsorption/desorption isotherms (Fig. 1) of both gold catalysts are typical of nanostructured materials (type IV according to the IUPAC classification) with the inflection point at p/p_0 between 0.2 and 0.4, depending on the sample. Not only N_2 sorption isotherms but also small-angle X-ray diffraction (XRD) patterns

(Fig. 2a) indicate the hexagonally ordered mesopores. The Au-metal crystallites were found for both Au-containing catalysts. The characteristic reflections of metallic gold at 2*Θ* =38.2° and 44.8° [8] are shown in the large-angle range of XRD patterns (Fig. 2b). The presence of metallic gold is confirmed by UV-Vis absorption band at ca 500 nm (not shown here).

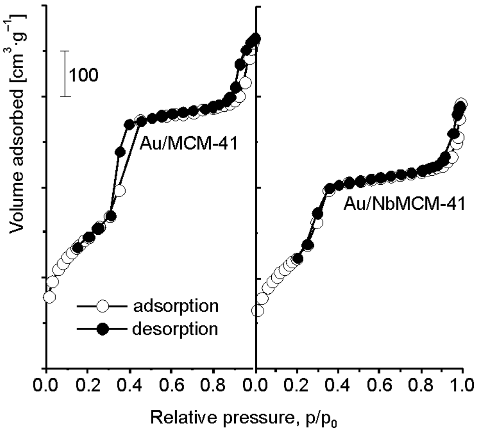

Fig. 1. N_2 adsorption/desorption isotherms of Au-containing MCM-41 materials

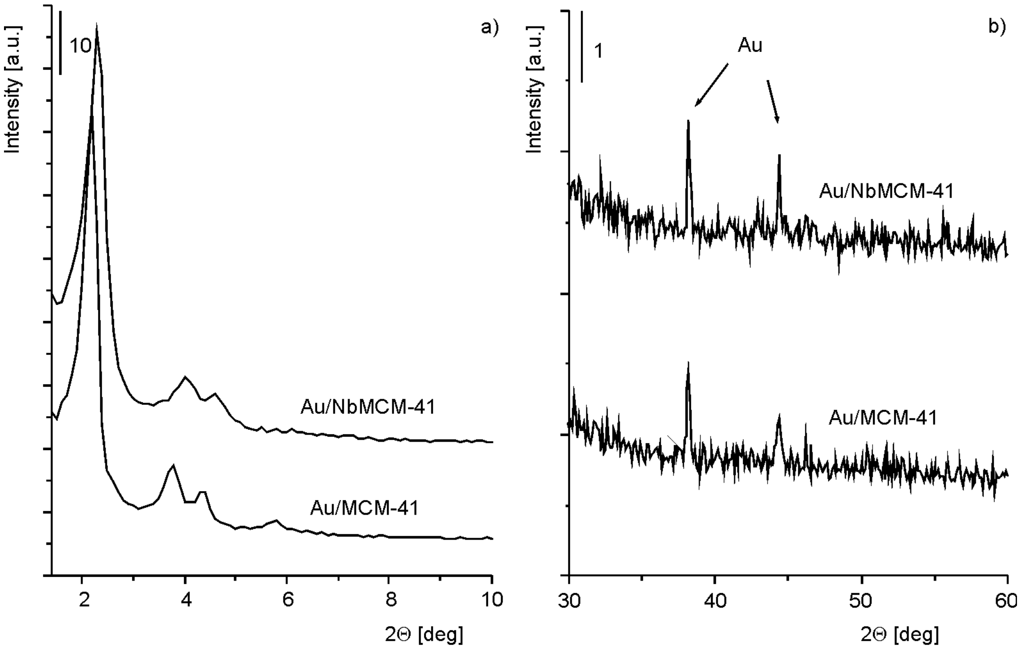

Fig. 2. XRD patterns of Au-containing MCM-41: small-angle (a) and large-angle (b) XRD range

UV-VIS spectroscopy appeared to be a useful tool for the determination of two cationic forms of copper in Cu-NaY zeolite (recorded at ca. 230 and 300 nm). Ni-NaY and Mn-NaY did not display cationic forms of metals detected by UV spectroscopy.

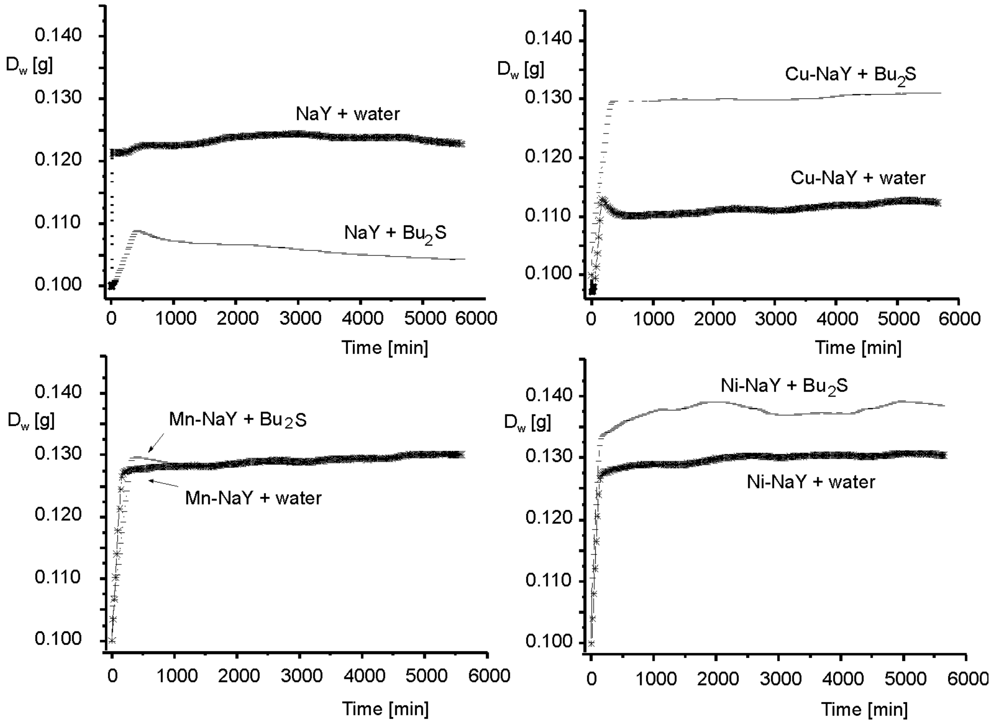

Fig. 3. Curves of water and Bu_2S adsorption at room temperature

Table 2. The amount of Bu_2S adsorbed on zeolites and MCM-41 materials

Adsorbent	Adsorbate	Wt. % of all adsorbates	Wt. % of Bu_2S
NaY	Bu_2S	22	0
Mn-NaY		15	1.5
Ni-NaY		25	0.8
Cu-NaY		25	6
Au/NbMCM-41		74	36
Au/MCM-41		70	37
MCM-41		56	9
NbMCM-41		52	17
NaY	$Bu_2S + H_2O$	29	0
Mn-NaY		30	0
Ni-NaY		29	0
Cu-NaY		29	0.2
Au/NbMCM-41		88	10
Au/MCM-41		87	6

The results of odour adsorption are presented as Bu_2S adsorption curves (Fig. 3) and as the amount of adsorbed compound after 7 days of adsorption in a desiccator (Tables 2, 3).

Table 3. The amount of $BuNH_2$ adsorbed on zeolites and MCM-41 materials

Adsorbent	Adsorbate	Wt. % of all adsorbates	Wt. % of Bu_2S
NaY	$BuNH_2$	30	4
Mn-NaY		30	10
Ni-NaY		34	14
Cu-NaY		40	15
Au/NbMCM-41		67	22
Au/MCM-41		71	24
NaY	$BuNH_2 + H_2O$	29	0.6
Mn-NaY		28	10.5
Ni-NaY		28	12
Cu-NaY		31	12
Au/NbMCM-41		81	18
Au/MCM-41		90	17

Zeolite sorption capacity ranges between 20 and 40 wt. %, depending on the nature of metal located in the structure, as indicated in Fig. 3. In the figure, the adsorption capacities have been compared for dibutyl sulfide and water. A high moisture content often has a negative effect on the adsorption process. It is especially the case of hydrophilic sorbents like NaY zeolite which preferentially adsorbs water not dibutyl sulfide. The same adsorption capacity for H_2O and Bu_2S was noted on Mn-NaY, whereas on Ni-NaY and especially on Cu-NaY, the amount of adsorbed sulfide was much higher than that of water. It is important that contrary to e.g., Mn-NaY, in Cu-NaY copper atoms occupy mainly cationic positions which strongly interact with dibutyl sulfide. When dibutyl sulfide was evaporated in a desiccator, in which the concentration of moisture increased by the location of the source of water vapour, the selectivity of sulfide adsorption decreased significantly (Table 2). Thus there is a high competition between adsorption of water and dibutyl sulfide. Contrary to these results, the adsorption of amine is not reduced by an increase of water vapour concentration (Table 3). It is clearly seen that the nature of transition metal is not a key point in the adsorption of butyl amine and that the selectivities of all transition metal-containing zeolites studied in this work towards amine sorption are much higher than that towards sulfide.

On the contrary, the sorbents based on mesoporous molecular sieves of MCM-41 type exhibit very high selectivity in sulfide adsorption. The role of gold in this behaviour is evident. The matrices without gold modification adsorb much less sulfide. The adsorption capacity towards sulfide does not depend on the nature of matrix (silicate MCM-41 or niobosilicate NbMCM-41) so long as the higher moisture content is not applied. In the latter case, the gold material based on NbMCM-41 support is more selective towards sulfide than Au/MCM-41. It is due to the lower hydrophilicity of NbMCM-41. The important advantage of mesoporous materials applied in this work is their extremely high total sorption capacity (> 70 wt. %) and sulfide sorption capacity (ca. 35 wt. %), giving a possibility of concentration of high amount of odours in a small amount of sorbent. The other advantage is an easy recovery of sorbents via oxidation of odours catalysed by gold dispersed on the mesoporous support [9, 10].

Adsorption of dibutyl amine (Table 3) on mesoporous sorbents is less selective (22–24 wt. %) than that of dibutyl sulfide but significantly higher than the sorption selectivity on zeolites.

4. Conclusions

Zeolites containing transition metal ions exhibit a higher selectivity in sorption of amines than in sorption of sulfides. Among zeolites, the highest amounts of odours are adsorbed on Cu-NaY. Zeolites are not selective towards dibutyl sulfide in a high moisture content. However, the most attractive sorbents are gold modified MCM-41 materials which not only adsorb the highest amounts of both odours but also are highly selective. Niobium located in NbMCM-41 matrix enhances the hydrophobicity of the material and increases the adsorption of odour in a high concentration of water vapour. Gold containing sorbents are easily regenerated via catalytic oxidation of sorbats.

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