

RESEARCHES CONCERNING THE UTILIZATION OF MICRO- AND NANO-POROUS MATERIALS BASED ON CLAYS AND ZEOLITES IN GASES DEPOLUTION

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Abstract This study underlines the utilisation of different micro- and nano-porous materials (clays, molecular sieves-zeolites) in depollution of industrial gases. The most commons polluted gases that results in industry are CO, CO₂, SO₂, NO_x, VOC (volatile organic compounds), NH₃ etc. Two of the most appropriate materials (low costs, good adsorption properties) that can be used in gas separation are based on different types of clays or zeolites. The major advantage of using clays and zeolites in gas separation is their potential ability for the successive regeneration and the lower temperature of reaction. This paper presents the results of the most recently studies regarding industrial gases depollution using porous materials based on clays and zeolites.

Keywords: depollution, clays, zeolites, polluted gases.

1. INTRODUCTION

Due to the intense industrial activity there were signalled increased quantities of polluted agents in industrial gases. There are known the noxious effects on environment and on human health of those; so, it is important to design adsorbent materials that can retain these gases before their liberation in the atmosphere and of some efficient methods of solid-gas contacting. Also, there were used a lot of natural or synthetically adsorbent materials for inorganic and/or organic species retaining: clays, zeolites, active charcoal etc. [1-3]. Yang and Baksh [4] were the pioneers in studies of the gas separation process by using clays minerals. Gas adsorption by chemically modified clays or zeolites has also been studied by Yang and Cheng [5] Venaruzzo et al [6], Volzone and Ortega [7] and others [8-13].

2. UTILIZATION OF CLAYS IN GASES SEPARATIONS

Clay minerals represent the major constituents of the clays raw materials and had been classified in seven groups according to their structure and crystal chemistry [14]: 1-the kaolinite and serpentine group, 2-the group of micas, 3-the vermiculite group, 4-the group of smectites, 5-the phyrophilite and talc group, 6-the group of chlorites and 7-the palygorskite and sepiolite group. Technological properties of clay raw materials depend strongly on the properties of the clay mineral present, total mineral composition, size distribution, degree of consolidation and processing conditions [14]. Clays appear to be the most interesting micro(nano) porous materials in terms of availability, widespread and properties [15].

Clay's minerals have a vast area of utilisation in environment protection because of their role as sorbents and retention-insulation materials. There were studied the adsorption properties of clays from the kaolinite group (typically two-sheet phyllosilicates) [7]. According to the literature, the mineralogical composition of the natural

kaolinitic clay has a great influence on gases adsorption (O_2 , N_2 , CO , CH_4 , CO_2 etc). Also, the treatment with mineral acids can improve the adsorption capacity of the natural kaolinite.

Another group of clays studied were the chemically modified bentonitic clays, utilized as adsorbents of CO , CO_2 and SO_2 gases [6]. Bentonites are smectitic clays (strongly expanding three-sheet phyllosilicates) with high adsorption capacities. According to the literature, the gases (CO and CO_2) retention is much higher (in bentonite cases) if the clay has a higher content of smectitic compounds, had a higher BET surface and a higher micropores volume. Treating the clay with a concentrated mineral acid (HCl or H_2SO_4) it can increase the number of Lewis and Bronsted sites and obtained a higher adsorption capacity for polluted gases.

Pillaring is a new method of clays internal structures chemically modifying that consist in intercalation and fixation (by calcinations) of bulky molecules (pillars), modifying the interlayer distance and creating a permanent porosity. The pore size (interlayer free spacing) can be changed by introducing pillars of different sizes. There were developed studies regarding the adsorption characteristics of hydrogen sulphide on montmorillonites modified with iron by pillaring techniques. Also, Nguyen-Thanh et al [10] concluded that the presence of iron species on the surface of clay matrix reveals a promising capacity for H_2S adsorption. Heylen et al. [16] relieve some methods that increase the adsorption capacity of Fe-PILC (pillared clays with iron) for CCl_4 , $CHCl_3$, CH_2Cl_2 and CH_4 , at $0^\circ C$. The first modification method consist on preadsorption of butylamonium ions between the clay sheets, the result is the increasing of the porosity and the adsorption capacity of the modified material. Another method is based on the incorporation of the Zr species into the Fe pillars forming Fe-Zr pillars with a higher interlayer free space.

Morissay F.A. et al studies relived that the capacities of the clay mineral particles to adsorb the VOC gases are significant (up to 15% of the original mass) and these capacities are relative to the specific surface of the particles [17].

3. UTILIZATION OF MOLECULAR SIEVES IN GASES SEPARATIONS

Due to the free spaces of the zeolitic framework that have the same dimensions like the critical dimensions of some molecules, the zeolites were surnamed “molecular sieves” [22]. There were performed a lot of studies of adsorption of CO_2 on various natural (mordenite, ferrierite, clinoptilolite, chabazite) and synthetic zeolites (ZSM-5, 5A etc); the result of these studies showed that chabazite to be a more promising adsorbent from CO_2 separation than 4A or other synthetic zeolites [19].

The adsorptive behaviour of CH_4 and CO in the pores of Ω -zeolite was investigated by Yamazaki et al [18]. They concluded that CO was preferentially adsorbed into the smaller pores and CH_4 was scarcely adsorbed in the smaller pores at temperature lower than 214 K.

Triebe and Tezel [20] studied the adsorption of N_2 , CO , CO_2 and NO on various molecular sieves (H-mordenite, synthetic zeolites 4A and 5A, natural clinoptilolite and activated carbon) using the gas chromatographic method to determine the potential for separation of these air contaminants from atmospheric air. The results of this study showed that the clinoptilolite yielded the strongest adsorption of NO , CO and N_2 in 323-473 K field. Also, they had demonstrated that CO_2 was strongly and irreversible adsorbed on the clinoptilolite and the diffusion of N_2 in clinoptilolite was three times greater than that of CO under the same conditions.

Ackley et al [21] tried to demonstrate that the utilization of the natural zeolites on gas separation is much advantageous in spite of the synthetic zeolites. Also, they present in their study [21] the great advantages and the small disadvantages of natural zeolite utilization: variable chemical composition and purity but a great thermal stability, higher stability to acid environments than many common synthetic adsorbents, low costs. Table 1 present the structural properties of the common natural zeolites with potential in gas separation processes.

Table 1. Structural properties of selected natural zeolites [21]

Natural zeolite	Si/Al	Major cations	Kinetic pore diameter, nm	Max H ₂ O capacity, kg/kg	Total pore volume, %
Chabazite	1.5-4	Na, Ca, K	0.43	0.28	48
Clinoptilolite	4-5.2	Na, Ca, K	0.35	0.14	34
Erionite	3-4	Na, , K, Ca	0.43	0.20	36
Ferrierite	4.3-6.2	K, Ma, Na	0.39	0.12	24
Mordenite	4.4-5.5	Ca, Na	0.39	0.15	26
Phillipsite	1.3-3.4	K, Na, Ca	0.26	0.22	30

4. CONCLUSIONS

Natural clays and zeolites present adsorption properties and can retain polluted gases from atmosphere and from industrial gases. For the enhancement of their adsorption capacity it can be used a lot of methods (that are presents in this paper) that modify the internal structure of the initial solid material. Utilised like native materials or chemically modified natural materials or artificial synthesized, clays and zeolites are materials with unlimited potential of environment protection utilization, for the separation of the polluted gases from atmosphere or for the purification of industrial gases before theirs reaching in the atmosphere.

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