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Characterization of some materials with porous structure

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Porous materials are commonly found in nature and as industrial materials such as carbon, silice, zeolites, alumina etc. In order to use them effectively, their mechanical and physical properties must be understood in relation to their porous structures. This paper studies the mechanical and physical properties of a few common porous materials: carbon, zeolites, alumina. The characterisation of pore structures was performed using a Mercury Porosimeter. Detailed information was obtained on the density, porosity, surface area and pore size distribution. Through X-ray diffraction, optic microscopy and transmission electon microscopy there were determined microstructure and crystallisation degree. Based on experimental observations we predicted the macro-properties from the micromechanis viewpoint. By studying the deformation of pores the global behaviour was estimated.The study has provided insight into the mechanical properties of advanced porous materials used as sorbents or as supports for making of catalysts.

1. INTRODUCTION

Porous materials have been widely used in practice. More and more such materials are produced using different technologies in order to achieve desired mechanical properties. The understanding of the relationship between the microstructure properties such as porosity and the global mechanical behavior is, however, far from satisfactory. Research in this area is receiving attention recently [1-4], including the properties of carbon [5-6], zeolitis, alumina [7].Recent discovery of a new family of mesoporous molecular sieves has been receiving much attention. Their synthesis and utilization have been investigated by many researchers because of their peculiar characteristics; large internal surface area, uniformity of pore size and easily controlled size of the pore. All these porous materials may be useful as adsorbents [8], supports [9] and catalysts[10].

In the recent years, activated carbon, zeolites, alumina have been utilized positively as an indispensable materials for removing pollutants and bad smells, etc., from air and water. The usage of activated carbon, zeolites and alumina is still increasing in industrial processes and civil life for the purpose of environmental preservation.

The main raw materials for making activated carbon are charcoal and wood which are very porous because they are plant tissues. Activated carbon made from these raw materials has pores of different size making the adsorption efficiency very high. Wood which has strong

plant tissue, can be considered to be a useful raw material for activated carbon. Therefore, activated carbon is being investigated as one of the recycling applications for wood [11-12].

Zeolite materials are built from three–dimensional silicate frameworks enclosing channels and holes. Through variations in the silicate framework, different types and sizes of channels and hole systems can be obtained, having different catalytic, ion exchange and molecular selection properties. Different synthetic zeolites are made and they show one-tow and three-dimensional channel systems, with channel diameters of 3;4;5;6;7;8;9;12 Å, respectively. The use of huge quantities as catalysts, ion exchanger and adsorption agents have moved these materials into one of the most important chemicals today.

This paper studies the mechanical and physical properties of a few common porous materials: carbon, zeolites, alumina. The characterization of pore structures was performed using a Mercury Porosimetrer. Using this technique, detailed information was obtained on the density, porosity, surface area and pore size distribution. A large number of experiments were conducted with compression setup and their macro-mechanical properties such as hardness and strength were obtained.

2. EXPERIMENTAL

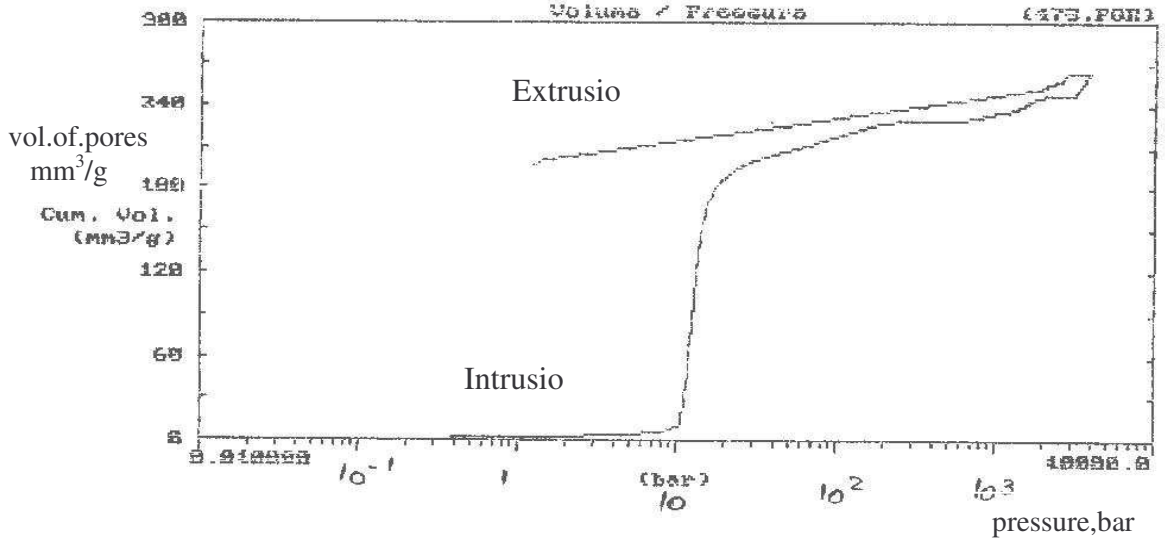
In order to prepare activated carbon it was used charcoal or walnut shells as the raw materials. These materials were carbonized in inerth atmosphere and the coke obtained was crhused and agglomerated with pitch and starch. The homogeneus paste was extruded in a pneumatic press to form of pellets. This carbonized product were treated by activation in nitrogen atmosphere at temperature of 750^0 C, for about 30 min.

Zeolite 4A is not found in nature as mineral and is obtained by hydrothermal synthesis from alkaline gels and aluminosilicates. Its usual shape is in sodium form, but through different ways can be obtained other cationic shapes of the mono, di or trivalent metals. Zeolite 4A was obtained from the mixture of sodium silicate, sodium aluminate, sodium hydroxide, water and natural kaolin by uniform mixing. The composition was put in a crystallizer tank and held for a few hours at a temperature of about 100^0 C. Thus, there were obtained zeolite crystals, which were separated from the base solution by a vacuum filter,then dried and calcinated.

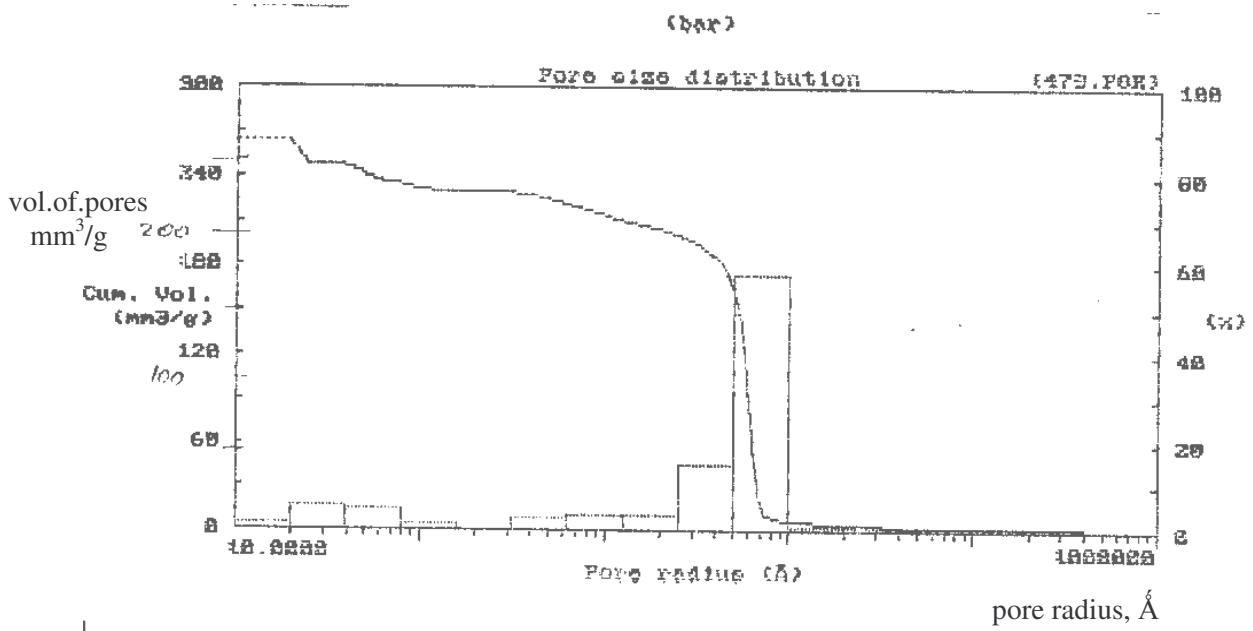
Production of spherical alumina supports are produced by a process in which a mixture of a alumina hydroxide hydrosol and organic monomers is introduced dropwise, through calibrated orifices, into a column of heated oil. Each drop of oil insoluble mixture forms a sphere of alumina, which are then carbonised at temperature of 600^0 C.

A mercury porosimeter (Carlo Erba) was used to characterise porous materials in terms of porosity and surface area. It is capable to generating a pressure up to 60.000 psi (4000 atm) detecting a range from micro to mezo and macro-pores. It has four low pressure parts and two high pressure chambers burring each test, mercury was forced into the porous samples by hydraulic pressure and the volume of mercury penetrating the pores was measured directly as a function of applied pressure. Mercury would intrude into big pores initially and then into smaller pores as the pressure increases.

Typical samples ware prepared to the size 3x3x1 mm. All samples were dried in oven to remove the water vapour. For high pressure runs the equilibrium time was set at 10-15 s. Figure 1 shows a typical intrusion-extrusion curves (a) and pore size distribution (b) for zeolite 4A. Specific surface areas were determined using the adsorbed quantity of nitrogen at the temperature of liquid nitrogen and were calculated from BET equation, expressed in m^2/g.



a) cumulative intrusion - extrusion curve for zeolite 4A



b) pore volume as a function of pore size

Figure1. Typical curves for zeolite 4A obtained from the mercury porosimeter a) cumulative intrusion vs. diameter; b) pore volume vs pore size radius.

The adsorption capacity was evaluated from the quantity of iodine adsorbed. Iodineadsorption capacity was measured by mixing 0.2 g of porous material (active carbon, zeolite or alumina) with 50 ml of iodine test solution (52 g of potassium iodate was dissolved in 30 ml water and after addition of 13 g iodine.

The total volume was adjusted to 1l, shaking the mixture for 15 min in a shaker, and then using centrifugation to sediment the porous material. The supernatant liquid was titrated with 0.1 mol/l sodium thiosulfate solution to obtain the concentration of remaining iodine.
From the difference in iodine concentration before and after the porous material (active carbon, zeolite or alumina) is mixed, the adsorbed quantity of iodine was calculated and the adsorption capacity was exppressed by the quantity of iodine adsorbed in mg/g of porous material.

Porous material (active carbon, zeolite or alumina) were tested for their resistance strength using a three point bending setup with an extrudate about 4 mm in diameter and 5 mm in lenght. From the maximum force attained the strength was calculated based on the elementary bending theory.

3. RESULTS AND DISCUSIONS

Three groups of porous materials were tested and analysed. They were active carbon, zeolite 4A (6x4mm extrudates) and pelletes of activated alumina (∅ 5-6mm).

All porous materials were obtained such as presented in paragraph 2. Within each group, materials of different porosity were obtained by changing processing parameters slightly. Table 1 contains the data for active carbon and zeolite 4A extrudates and spherical activated alumina.

Table 1
Test results for active carbon, zeolite 4A and activated alumina (activation temperature: 750^0C for active carbon, and 600^0C for zeolite 4A and alumina)

Sample	Porosity %	Surface area (m^2/g)	Density (g/cm^3)	Hardness GN/m^2	Fracture Toughness (kgf/mm^2)	Median pore diameter (Å)
Activated carbon CH	42	970	0.47-0.53	16.06	2-3	26-200
Activated carbon CW	55	840	0.51-0.55	14.78	2-3	30-280
Zeolite 4A	30	197	1.28	42.55	2-4	4-6
Activated alumina	38	280	0.90	29.74	3-5	45

From table 1 it can be seen that strength values decrease when porosity increase, as expected. It is interesting to note the different values of sthength for active carbon are considerably lower then zeolite and activated alumina. Porosity has been selected as a key parameter and data in table 1 are plotted in a similar way as shown in figure 2. A similar trend of effect of porosity on the mechanical properties is observed. The raw material used for to prepare porous active carbon was considered to reflect the difference in porosity of the carbonized products from the charcoal and walnut shell char such as shown in table 1, that is, the higher porosity of carbonized product accelerates the permeation of gas into the interior of the carbonized products, and also the evacuation of gas which was generated by the activation reaction. The adsorption capacity of porous materials depends on the size of the effective adsorption area and the quantity of adsorption caused by capillary condensation. Therefore,

the surface area has a large effect on the adsorption capacity. The increase of specific surface area may be due to the development of microporose on the surface of activated product by the activation treatment. The reduction of specific area may be due to the destruction of micropores formed on the surface of porous material and for active carbon the increase in ash of activated carbon, because of the material activation temperature he excess activation treatment.

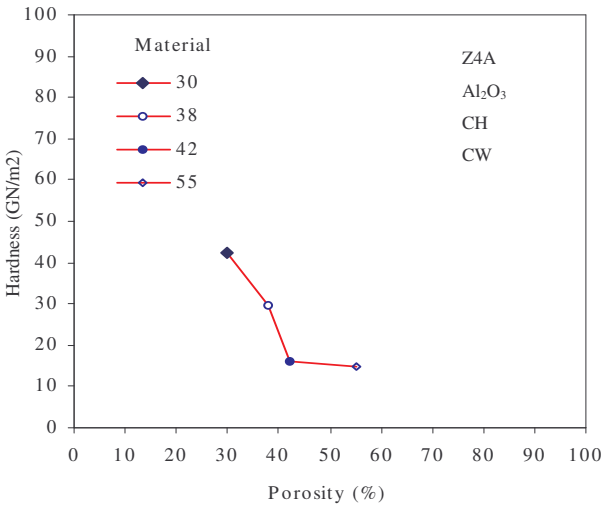


Figure 2. Plot of hardness vs. porosity of the material

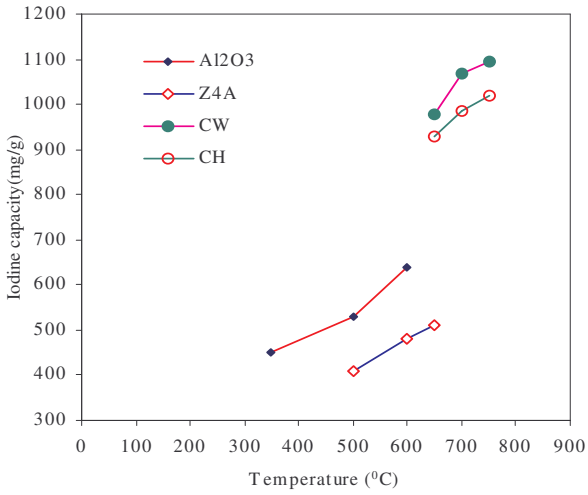


Figure 3. Iodine adsorption capacity vs. activation temperature

The adsorption capacities for iodine are influenced by the type of porous material and the activation temperature and depends of the raw material used as start material. The iodine adsorption capacity increases linearly if the specific surface area increased, figure 4.

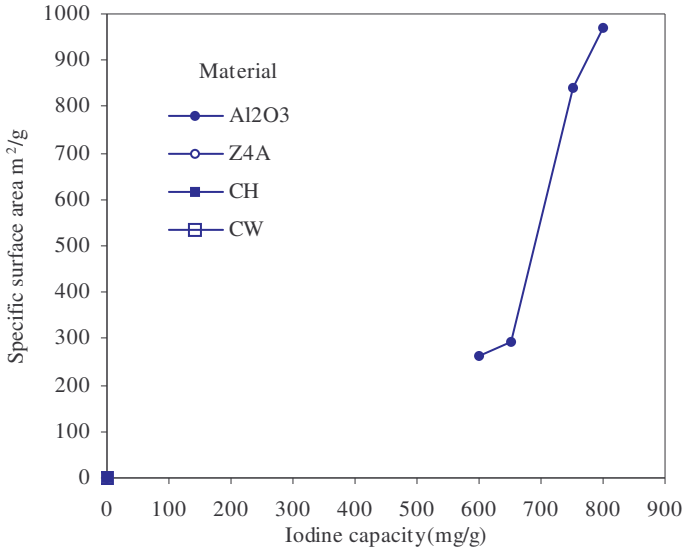


Figure 4. Relationship between specific surface area and iodineadsorption capacity.

The iodine adsorption capacity is influenced by the activation temperature. The iodine adsorption of carbon activated at 750^0C was better than that of carbon activated at 600^0C. The iodine adsorption capacity in relation to the specific surface area was also influenced by the activation temperature and depends of the raw material used as start material.

4. CONCLUSIONS

The specific surface area and porosity of the investigated materials are influenced by activation temperature. Low density was caused by low temperature, and high specific surface area and high porosity was caused by higher temperature.The adsorption iodine capacity was very different, material with higher porosity presented greater adsorption capacity. The best result was obtained from activated carbon that is much more porous material then zeolite and alumina.The iodine adsorption capacity was influenced by activation temperature and specific area.Besides the porosity, preparation conditions do affect the sintering and, therefore, the mechanical properties. As the porositry increases, the strength and hardness decrease substantially. For the materials which were investigated the hardness was increased as follows: activated carbon > alumina>zeolite.

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