

# KINETICS OF AIR ADSORPTION ON CMS STUDIED BY TPD-MS-SMB

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## Introduction

Carbon molecular sieve fibers (CMSF) are characterized by the existence of constrictions in series and wider pores in between [1]. The major part of the pore volume are composed of wider pores some of them are in restricted regions. The constrictions which are responsible for the molecular sieving effect are, on one hand, low energy sites, because of steric interactions of both pore walls with the adsorbate molecules, but on the other hand, these sites are much less accessible [2]. At room temperature permanent gases like nitrogen and oxygen have sufficient energy to penetrate obstructed regions and the minute amount adsorbed are located mainly on these low energy sites [3]. The role of the physical adsorption of air mixture ( $O_2$ ,  $N_2$ , and  $H_2O$ ) at room temperature on CMSF will be studied by the TPD-MS-SMB system.

## Experimental

The experimental setup is shown in the previous abstract. It is based on supersonic molecular beam sampling method, which bridge between the atmospheric TPD and the quadrupole mass spectrometer. The sample is place in silicosteel tube. Megabore column connects the sample inlet to the supersonic nozzle. He at 99.999% purity at flow of 30 cc/min and atmospheric pressure is introduced through the sample to the nozzle and expands to vacuum. The supersonic expansion is skimmed and enters to QMS fly-through.

The CMSF are TCM 128, used as received, produced by Carbone-Lorraine, France.

## Results and discussion

A typical TPD spectra of as received TCM 128 cloth exposed to air is shown in fig. 1. Oxygen, nitrogen and carbon dioxide desorption were simultaneously measured and presented in the figure while water

desorption is presented in fig.3 in the previous abstract.

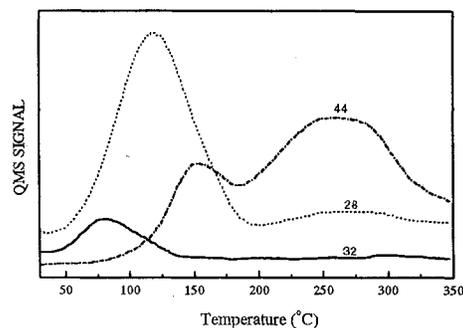


Fig. 1 TPD of nitrogen, oxygen and carbon dioxide from CMSF. The heating rate was  $30^\circ/\text{min}$ . The sample weight was 25 mg.

$CO_2$  is emitted as a results of the decomposition of surface oxides while,  $O_2$  and  $N_2$  are physically adsorbed, at room temperature, on the carbon surface. The source of the  $CO_2$  are probably the less stable carboxyl groups [4] since it start to decompose at relatively low temperature, about  $150^\circ C$  [5,6]. The high sensitivity and the fast respond of the TPD-MS-SMB system enable to clearly see 2 sites of oxide groups which decomposed to  $CO_2$  up to  $350^\circ C$ . In previous studies [5,6] no such high resolution spectra could be detected.

$N_2$  is physically adsorbed on the CMSF at room temperature. Since the TPD detector is a mass spectrometer, the mass 28 could be either  $N_2$ , CO, or fragment of  $CO_2$ . Therefore, in order to identify the signal at mass 28, the spectra of mass 14 is also measured. The MS spectrum of nitrogen contains also a small peak of mass 14, about 6% of the intensity of mass 28. CO contribution at that mass can be only due to molecular double ionization which found to be at much lower probabilities. The large nitrogen peak (mass 28) in the TPD spectra (fig 1.) have a corresponding mass 14 peak of about 5% of mass 28 intensity which indicates that the peak

correspond to nitrogen. A crossed check was done by gathering the gas evolved from a 1g sample heated to 200°C into a calibrated volume, followed by GC analysis.

In Fig.2 the kinetics of adsorption of air on CMSF at room temperature is plotted. The samples were evacuated for 16 hours at  $10^{-6}$  Torr and then were transferred into a desiccator with air atmosphere which contains water vapor at constant relative humidity of 62%. Oxygen and nitrogen could not be detected in the TPD spectra of CMSF measured immediately after the evacuation. The samples passed a TPD experiment as a function of exposed time in the desiccator atmosphere. Each experiment gives one point on the adsorption kinetics graph for the amount adsorbed of  $N_2$ ,  $O_2$  and water. The amount adsorbed were calculated by integrating the surface beneath the TPD peaks of  $N_2$ ,  $O_2$  and water, from spectra like those presented in Fig. 1. There was no change in the  $CO_2$  spectrum after evacuation at room temperature in all spectra, which indicates that evacuation at room temperature does not destroy oxide groups.

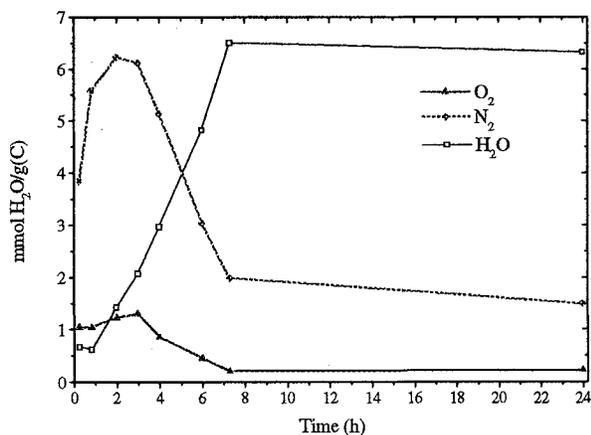


Fig. 2 Kinetic adsorption of  $O_2$ ,  $N_2$ , and  $H_2O$  on CMSF at air at constant relative humidity of 62%. The Y axis is calibrated for water. The  $N_2$  and  $O_2$  amounts are in arbitrary units.

From the adsorption kinetics of fig. 2. It could be seen that:

The amount adsorbed of nitrogen and oxygen passed through a maximum and then decreased to much lower level while the amount of water as a function of time steadily increased to high amount adsorbed.

Oxygen reach its high adsorption level before nitrogen and both of them are much faster than water adsorption.

Water reached its high adsorption level when oxygen and nitrogen completed their desorption.

It is well known that the effective diameter of oxygen is smaller than nitrogen [1] and in activated transport oxygen is permeating faster than nitrogen. As seen in Fig.2 the adsorption rate of  $O_2$  is faster than  $N_2$  and reach 90% of its maximum amount adsorbed after 15 min. (the first point of measurement) while  $N_2$  at that time reach only about 60%.

As for water molecules Fig.2 shows that when the evacuated carbon is exposed to a mixture of these molecules water is by far the slowest molecule to penetrate the pores. At relative humidity of 62% the water pressure is in the plateau region of the water isotherm where pore filling occurs. When the water molecule do adsorbed they push away the minute amount of both oxygen and nitrogen. Water adsorption starts on oxide sites, then it spreads to the entire surface through hydrogen bonding.

The influence of the relative humidity and the evacuation temperature of CMSF on the adsorption kinetics of nitrogen and oxygen and water vapor will be shown.

## Conclusion

The high sensitivity TPD-MS-SMB system enable to understand the mechanism of the simultaneous physical adsorption of nitrogen, oxygen and water on carbon fibers.

## References

1. J.E. Koresh and A. Soffer, J. Chem. Soc.Faraday Trans.I, 1980,76, 2457.
2. J.E. Koresh, T.H. Kim and W.J Koros, J. Chem. Soc.Faraday Trans.I, 1989,85, 1537.
3. J.E. Koresh, J. Chem. Soc.Faraday Trans, 1993,89, 2059.
4. H. P. Boehm, Carbon, 1994,32, 759.
5. S.S. Barton, D. Gillespie and B.H. Harrison, Carbon, 1973, 11, 649.
6. I. Mochida, S. Yatsunami, Y. Kawabuchi and Y. Nakayama, Carbon, 1995, 33, 1611.