FREQUENCY RESONANCE STUDIES ON METAL-DOPED NANOPOROUS CARBONS

György Onyestyák,[a] Aranka Pilbáth[b], Krisztina László[b]

[a] Institute of Nanochemistry and Catalysis, Chemical Research Center, Hungarian Academy of Sciences, P. O. Box 17, Budapest, Hungary, H-1525

[b] Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, Budapest, Hungary, H-1521

Introduction

Metal impregnation is widely used as a means of improving the ability of porous carbons to adsorb highly toxic chemicals from gas streams and are used in a variety of respiration and collective filter applications. They are effective in removing toxic gases and/or vapours in military, industrial and other applications.

New applications or restrictions may call for the development of novel salt compositions or impregnation methods. Before the application the new carbon materials have to pass a set of standard methods and most of them require a large sample size. However, the carbon samples in the early stage are often prepared in quantities less than the amount needed for the standardized break-through tests. Our intention is to study the so called frequency-response (FR) method as a possible substitute for the break-through test in this stage, in order to estimate the influence of the metal treatment on the sorption properties [1]. The FR technique is a transient method, where the equilibrium of the gas-solid system is periodically perturbed by changes in volume and the pressure response wave is recorded. The FR rate spectra are obtained by Fourier transformation, plotting the real and imaginary components of the complex response functions against the perturbing frequency. The response is influenced by several characteristics of the system, e.g., particle size, pore size distribution, surface chemistry. A resonance signal (peak and step) appears in the rate spectrum at the frequency that corresponds to the time constant of a transport process [2]. The technique can be used to determine the mechanism of the rate-governing step and the dynamic parameters of the transport processes.

In this contribution we report the use of FR method to investigate the performance of commercial and laboratory-made metal-doped carbons with model toxic industrial chemicals (TIC). Nonpolar organic, acidic and basic test molecules, propane, hydrogen sulfide and ammonia, respectively, were probed.

Experimental

The metal-free and impregnated commercial carbons used in these experiments were kindly provided by Norit. Laboratory-made carbons were prepared from polymer or lignocellulosic precursors and impregnated with copper, and/or zinc and/or molybdenum.

The kinetic properties of the metal-doped carbons were studied by FR rate spectroscopy in the frequency window 0.001-10 Hz. The batch-type FR system, as described in [1], was used. NH3, H2S and propane probe molecules were equilibrated in the FR apparatus at 30 °C and 133 Pa after pre-treatment of the carbon samples in UHV at 383 K for 1 hours.

Results and discussion

In the response curve the intercept of the sigmoid curve with the vertical axis is related to the amount of the adsorbed gas, while the time constant t characterizes the dynamic properties of the carbon towards the probe gas. Lower time constant means faster diffusion, as $t \sim \frac{r^2}{D}$, , where r is the radius of the pore and D is the transport diffusion coefficient.

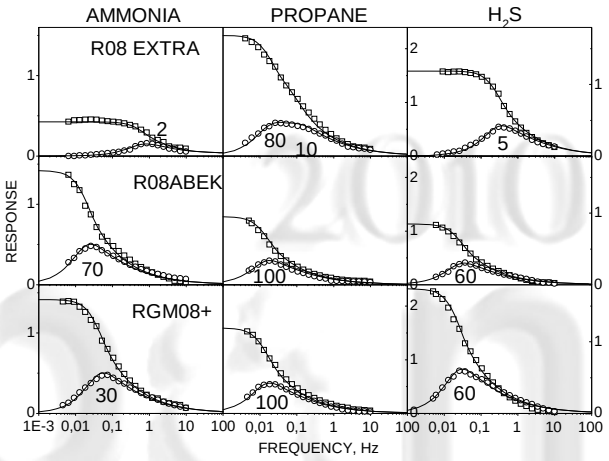

Fig. 1. FR curves obtained on the Norit carbons. The signal is normalized to 50 mg for propane and 200 mg for the other two gases. The numbers show the corresponding *t* values in s.

Fig. 1 shows that the surface treatment with metal salts influences both the adsorption capacity at 133 Pa and the diffusion. Propane uptake is reduced, and the diffusion is slightly slowed down. RGM08+ exhibits equally improved properties for both NH_3 and H_2S, as the adsorbed amount increased and the longer time constants show a longer residence time on the surface. From the shapes of the curves it also can be concluded that diffusion, rather than sorption, is the rate determining step.

In Fig. 2 we compare the response curves with the three gases on a metal-free high surface area polymer-based carbon and on the same carbon after the being treated with the metal salts.

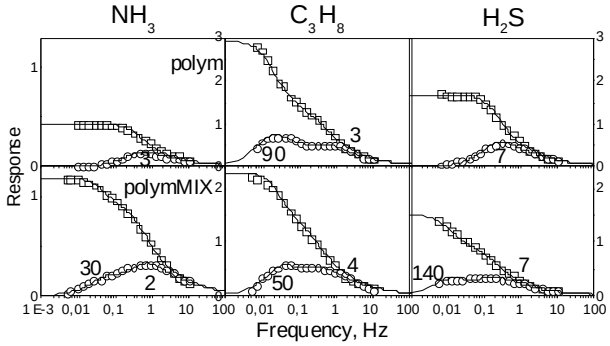

Fig. 2. FR curves on polymer based carbons without (polym) and with metal salt (polyMIX). The signal is normalized to 50 mg for propane and 200 mg for the other two gases. The numbers show the corresponding t values in s.

In the systems in Fig. 2, the highest the improvement in uptake for NH_3, while that of propane and H_2S are slightly depressed. At the same time, for both NH_3 and H_2S a significantly longer time constant was achieved.

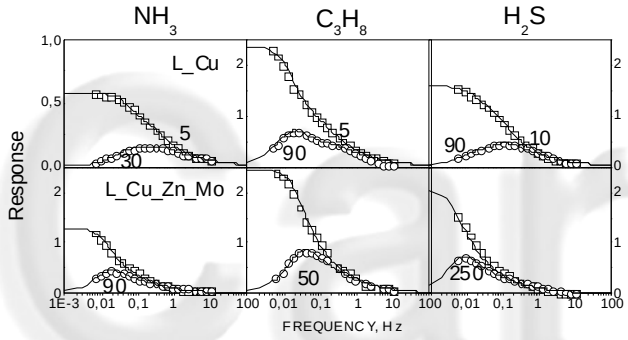

Fig. 3. FR curves on lignocellulose based carbons treated with Cu (L_Cu) and with Cu, Zn and Mo (L_Cu_Zn_Mo). The signal is normalized to 50 mg for propane and 200 mg for the other two gases. The numbers show the corresponding t values in s.

According to the curves in Fig. 3 the introduction of the additional metals improved the sorption and the retention of both the inorganic gases without practically influencing the behaviour towards propane.

Conclusions

The FR technique provided reasonable information about the sorption interaction of metal-doped porous carbons with inorganic and organic toxic materials. As the trends observed display good agreement with those obtained from classical break-through methods, this method can be used for screening the performance of carbon sorbents in the development stage. A further advantage of the method is that it needs a much more limited sample size than the break-through method, which is absolutely necessary for the final evaluation.

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References

[1] Rees LVC, Shen D. Characterization of microporous sorbents by frequency-response methods. Gas Sep. Purif. 1993;7:83-89.
[2] Yasuda Y. Frequency-response method for investigation of gas-surface dynamic phenomena. Heterog. Chem. Rev. 1994;1:103-124