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Surface properties of solid materials measured by modified inverse gas chromatography

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ABSTRACT

A novel modified inverse gas chromatography (IGC) method has been developed to investigate the surface properties of solid materials. On the modified IGC system, the every adjusted retention time of miscellaneous probe molecules can be rapidly calculated within only one sample injection through wisely induction a capillary column and two detectors, i.e., flame ionization detector (FID) and thermal conductivity detector (TCD). In the system, the relative dead time can be acquired from FID detector while the retention time can be obtained from TCD detector simultaneously. The significant advantage of our design is that, experimental time is greatly saved compared to the traditional IGC. In addition, the new system is capable of distinguishing variety surface properties of porous materials. Two types of active carbon samples were tested, and the results showed that their thermodynamic parameters were quite different, indicating that the samples have opposite acidic/basic properties. The use of IGC would be an effective tool to evaluate the physiochemical data of solid materials.

1. Introduction

The fundamental understanding of interface reactions is of great importance but also remains a great challenge. Both theoretical and practical studies of the inverse gas chromatography (IGC) have been growing rapidly in the field of interface reactions between probe molecules and solid materials [1–10]. IGC, an extension of the conventional gas chromatography, is testified to be not only a powerful and valued technique to determine the surface properties and thermodynamic functions for the adsorption of various organics probes in the Henry area [6,10,11], but also a fast and reliable technique to study the surface energies of polymers, copolymers, biopolymers, fibers, coatings etc. [11–13]. This is attributed to the fact that IGC is capable of comparing the surface nature of particulate samples, which is a difficult task for conditional method [14]. The specific surface area, for example, is normally determined by using standard Brunauer–Emmett–Teller (BET) method, but this method is unavailable to measure the adsorptive capacity of adsorbent. As a result, IGC has become a widely used technique to characterize surface, in particular, the surface Lewis acidic & basic property [15,16].

However, one limit of IGC is that only single-component probes can be performed in each injection when measuring the surface properties of solid materials [17]. The normal IGC should effectively avoid the multi-components probes directly through the strong adsorbents in the packed column and thus difficult to separate. Compared with the normal IGC, the modified IGC is equipped with a capillary column to separate multi-components probes, thus, it is more flexible and simple. In this article, a novel modified IGC system was developed and the thermodynamic surface properties of active carbons were characterized. The study directly assessed the effects of various volatile molecular probes on the surface of an active carbon sample and investigated their surface properties. Both the stationary phase and the separation of probes were studied. Based on the results, the modified IGC system is capable of measuring the single-component probes as well as the multi-components ones. As to our knowledge, it has not been reported that a modified IGC system with our design is constructed to evaluate surface properties of solid materials. With our approach, the modified IGC system can be widely applied to characterizing surface properties of solid materials, such as catalysts, minerals, fibers, etc.

2. Modified inverse gas chromatography (IGC) method

Fig. 1 shows the schematic diagram of the modified IGC system. The necessary component of this system is a standard Agilent 6890 gas chromatograph (GC), equipped with a selected capillary

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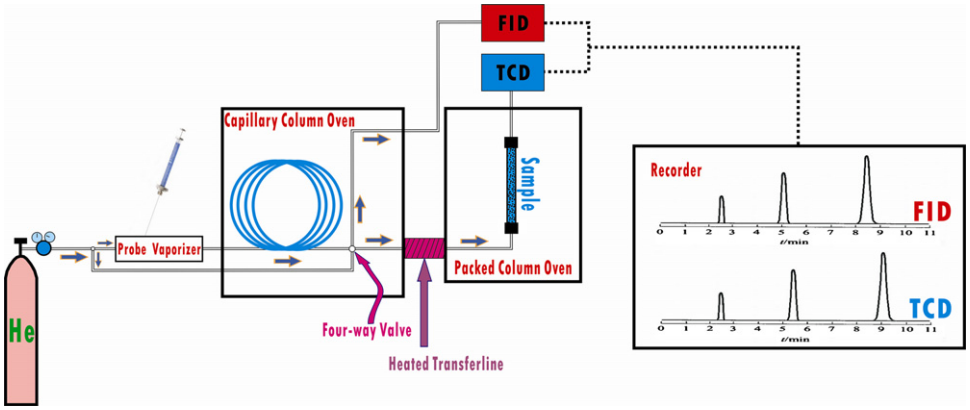

Fig. 1. Schematic diagram of the modified IGC system.

column and a short packed column. The channels of the four-way valve are connected, in turn, to the inlet carrier gas to enlarge the flow of carrier gas, FID detector, and the export of capillary column and the import of the packed column. Thermal conductivity detector (TCD) is connected to the packed column, thus, allowing us to analyze the adjusted retention time of probe molecules through the packed column. The micro-crosspiece is made by GERSTEL Company (Germany).

One point worth mentioning is that an external capillary column is employed in the configuration to meet the need of separation of the multi-components probes under an appropriate temperature programmed condition. The investigated samples (stationary phases) were placed in the packed column and the packed column was located in another temperature-controlled cabinet. Two respective temperature control systems allow setting different programmed temperatures on two types of column. The properties of investigated samples were determined based on the retention behavior of selected molecular probes. The adjusted retention time was measured according to the temporal difference between FID and TCD. The retention data were collected at maximum sensitivity. In the infinite dilution region injection of minor amount of adsorbents to approach zero surface coverage, the adsorption data obeyed the Henrys' law [11,18] and this system could be used for data collection over a wide temperature range. The automated injection valve was configured to inject the vapor of the mixture (appropriate mix of exultant vapor and carrier gas) into the gas flow, which transport the vapor through the column to the detectors. The multi-components probes were separated by the selected capillary column. Through a four-way valve, partial vapor that arrived at the FID detector can be used to determine the relative dead time and the rest was transferred over the investigated packed sample by carrier gas, and consequently entered into the TCD detector to determine the retention time.

3. Results and discussion

Our modified IGC was employed to study the surface properties of two types of active carbons [28,29]. Detailed experimental section is in the Supplementary data and detailed mathematical justification is in the Appendix. We adjusted and selected a suitable volume of sample to pack in the packed column. CH_4 was introduced to test the dead time [28], and the result showed that the dead time investigated by FID and TCD was exactly the same. It worth pointing out that the constant in the Formulas A4–A6 (in the Appendix) was zero. At this time, the retention time observed from the FID equaled the dead time. The BET areas of those active carbons were 898 m^2/g (denoted as C-1) and 1072 m^2/g (denoted as C-2), respectively. *n*-Alkane was employed to study the dispersive components of surface free energy of two

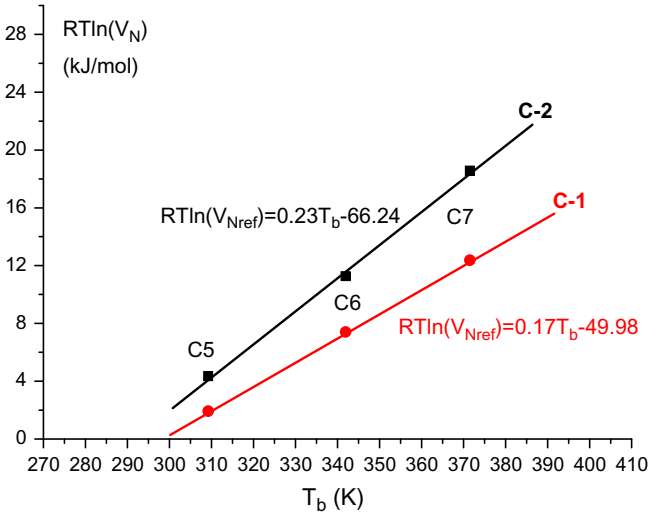

Fig. 2. Plots of RTlnV_N (kJ/mol) for the adsorption of *n*-alkane probe molecules on active carbons versus boiling point (T_b).

active carbons (Fig. S1 in the Supplementary data). Net retention volumes (V_N) and relative RTln(V_N) data are listed in Table S1–S4 (in the Supplementary data). Then, the molar free energy of adsorption of one methylene group ($\Delta G_a^{CH_2}$) adsorbed on the surface of active carbons can be calculated, and the values are −5.25 kJ/mol on C-1 and −7.10 kJ/mol on C-2. By Formula A9 (in the Appendix), the dispersive components of surface free energies ($\Delta\gamma_S^D$) of the active carbons are −154.1 mJ/m^2 on C-1 and −282.2 mJ/m^2 on C-2. The results well indicate that the lower the dispersive component of surface free energy is, the stronger adsorption ability of the active carbon is. The strong adsorption ability comes from high BET area of active carbon [28]. Of course, this reason can also well explain the difference of the molar free energy of adsorption of one methylene group ($\Delta G_a^{CH_2}$) adsorbed on the surface of active carbons.

In order to investigate the enthalpy of the specific adsorption (ΔH_a^S), the acid constant (K_a) and the base constant (K_b), the values of RTln(V_{Nref}) of polar probe molecules, which has the same boiling point as the relative *n*-alkane, should be studied [27]. RTln(V_N) of the *n*-alkanes as a function of boiling points (taken from the NIST chemistry book in Table S5 in the Supplementary data) shows a good linear relationship, as shown in Fig. 2. The formulae of the linear relationship as follows:

$$RT\ln(V_{N_{ref}}) = 0.17T_b - 49.98 \quad (1)$$

$$RT\ln(V_{N_{ref}}) = 0.23T_b - 66.24 \quad (2)$$