Macromol. Symp. ***194***, *27–37 (2003)*

Inverse Gas Chromatography in the Examination of Modified Fillers

Adam Voelkel

Poznań University of Technology, Faculty of Chemical Technology, Institute of
Chemical Technology and Engineering, pl. M. Skłodowskiej-Curie 2, 60-965
Poznań, Poland

Summary: Dispersive and specific surface properties of silica modified with silanes, titanium and zirconium coupling agents were characterised by means of inverse gas chromatography. This method was also successfully applied in the examination of raw and modified silicates.

Introduction

Inverse gas chromatography has become an accurate, reliable and fast method for the physicochemical characterisation of polymers and their blends, fibres, modified silica and other surfaces, surfactants, as well as, commercial stationary phases and their mixtures and petroleum pitches, heavy residues of oil distillation. This technique has been also used to study of water sorption ability of different materials. The term "inverse" indicates that the examined material, e.g. polymer blend or modified silica, placed in the chromatographic column, are of interest in contrast to the common analytical gas chromatographic experiments. Carefully selected test solutes are injected into the flow of a carrier gas and transported over the surface of e.g. fiber. The retention time and the peak elution profiles of standard solutes, affected by interactions between the solute and stationary phase, are used to estimate those interactions.[1,2] Applications of IGC were presented in several reviews[3-5] and number of individual papers.[6-18]

Intermolecular interactions in an adsorbent-adsorbate system may be generally divided into dispersive and specific. Thus, the free surface energy (γ_s) has two components - specific (γ_s^s) and dispersive (γ_s^d) according to equation (1)

$$\gamma_s = \gamma_s^d + \gamma_s^s \qquad (1)$$

The standard free energy of transferring a mole of vapour from the gas phase to a standard state on the surface, i.e. the adsorption energy, is given by

CCC 1022-1360/00/$ 17,50+.50/0

$$\Delta G^0 = -RT \cdot \ln \frac{B \cdot V_N}{S \cdot g} \tag{2}$$

where B=2.99•10^2, S is the specific area of the adsorbent, g is the mass of the adsorbent in the column, and V_N is the net retention volume.

For a given system equation (2) changes into

$$\Delta G^0 = -RT \cdot \ln V_\mathrm{N} + \mathrm{const} \tag{3}$$

The adsorption energy has two components: specific (ΔG^s) and dispersive ((ΔG^d) according to equation (4)

$$\Delta G^0 = \Delta G^\mathrm{d} + \Delta G^\mathrm{s} \tag{4}$$

For n - alkanes $\Delta G^\mathrm{s} = 0$ and $\Delta G^0 = \Delta G^\mathrm{d}$. The ΔG^d changes with the number of carbon atoms in their molecules. Its increment corresponding to a methylene group may be calculated from equation (5)

$$\Delta G_{CH_2} = -RT \cdot \ln\left(\frac{V_{N,n}}{V_{N,n+1}}\right) \tag{5}$$

where $V_{N,n}$ and $V_{N,n+1}$ denote the net retention volumes of n-alkanes having n and n+1 atoms respectively.

According to Dorris and Gray[19]

$$\Delta G_{CH_2} = 6.023 \cdot 10^{23} \cdot a_{CH_2} \cdot 2\left(\gamma_\mathrm{s}^\mathrm{d} \cdot \gamma_{\mathrm{CH}_2}\right)^{1/2} \tag{6}$$

where a_{CH_2} denotes the surface covered by one methylene group (0.06 nm^2) and γ_{CH_2} is the free surface energy of polyethylene.

Usually γ_{CH_2} is equal to 35.6 [mJ/m^2] or is calculated as $\gamma_{\mathrm{CH}_2} = 35.6 + 0.058 \cdot (293 - T)$.

The dispersive component of surface free energy can be calculated from equation (7) with the use of experimentally determined ΔG_{CH_2} values:

$$\gamma_s^d = \frac{\Delta G_{CH_2}}{4 \cdot (6.023 \cdot 10^{23})^2 \cdot a_{CH_2}^2 \cdot \gamma_{CH_2}} \tag{7}$$

Specific properties

The acid-base properties of the examined surface can be determined after calculating the specific component of the adsorption energy, *(*ΔG^s*)*. From its temperature dependence one may calculate the enthalpy of specific interactions *(*ΔH^s*)* which is used to calculate the acid-base properties of the examined surface. The acid-base properties of the examined surface can be determined after calculating the specific component of the adsorption energy, ΔG^s. From its temperature dependence one may calculate the enthalpy of specific interactions ΔH^s which is used to calculate the acid-base properties of the examined surface. The specific component of the adsorption energy, ΔG^s, calculated as a difference between the adsorption energies of polar test compounds and a hypothetical n-alkane having the same dispersive or other properties. Saint Flour and Papirer[8] proposed the use of the logarithm of the saturated vapour pressure ($log\, p^o$). Thus the specific component of the adsorption energy, ΔG^s, according to Papirer can be calculated by subtracting from the adsorption energy ΔG of a polar probe the adsorption energy of a hypothetical n-alkane having the same value of the logarithm of the saturated vapour pressure ($log\, p^o$). However, this parameter can be determined with the use of the number of the parameters describing the reference state. The specific component of the adsorption energy, ΔG^s, is calculated for all polar probes at different temperatures. The specific component of the enthalpy of adsorption, ΔH^s, is then can be obtained from the temperature dependence of ΔG^s.

The specific component of enthalpy of adsorption ΔH^s is further correlated to parameters characterising surface ability to specific interactions[20]

$$-\Delta H^s = K_D \cdot AN^* + K_A \cdot DN \tag{8}$$

where ΔH^s is the enthalpy of specific interactions, AN^* and DN are the acceptor and donor number of the test solute, K_A and K_D reflect the ability of the examined surface to act as electron acceptor and electron donor, respectively.

The parameters K_A and K_D are calculated with the use of the transformed equation (9). For example when calculating K_A the equation (8) changes into

$$\frac{\left(-\Delta H^s\right)_i}{AN_i^*} = K_A \frac{DN_i}{AN_i^*} + K_D \tag{9}$$

where index ‘i’ means the value of any parameter for different test compounds.

The properties of the monomolecular layer may be determined by the solubility parameter what is defined as the square root of the cohesive energy density.[21]

Guillet and DiPaola-Baranyi[22] proposed to calculate the solubility parameter for species with low volatility by using the solute-solvent interaction parameter $\chi_{1,2}^{\infty}$ given as

$$\chi_{1,2}^{\infty} = \ln\left(\frac{273{,}15R}{p_1^0 V_g^0 M_1}\right) - \frac{p_1^0}{RT}\left(B_{11} - V_1^0\right) + \ln\left(\frac{\rho_1}{\rho_2}\right) - \left(1 - \frac{V_1^o}{V_2^o}\right) \tag{10}$$

where M_1, p_1^0, B_{11}, V_1^0, ρ_1, and V_g^0 are the molecular mass, saturated vapour pressure, second virial coefficient, molar volume, density and specific retention volume of the solute, respectively; ρ_2 and V_2^0 are the density and molar volume of the stationary phase, respectively, T is the column temperature and R is the gas constant. Indices "1" and "2" refer to "test solute" used in IGC experiment and examined material, respectively.

The solubility parameter δ_2 may be calculated from the following equation

$$\frac{\delta_1^2}{RT}-\frac{\chi_{1,2}^{\infty}}{V_1^o}=\frac{2\delta_2}{RT}\delta_1-\left(\frac{\delta_2^2}{RT}+\frac{\chi_s^{\infty}}{V_1^o}\right) \tag{11}$$

in which δ_1 and δ_2 are solubility parameters of the test solute and the examined material, respectively.

For the series of test solutes (having different δ_1 values) retention data are collected and the respective values of the solute-solvent interaction parameter are calculated (equation 10). Having the set of $\chi_{(1,2)i}^{\infty}$ and δ_{1i} values for the respective test solutes one may calculate the slope of linear relationship: left hand-side (LHS_i versus δ_{1i}). One should use the following version of the earlier equation:

$$\frac{\delta_{1i}^2}{RT}-\frac{\chi_{(1,2)i}^{\infty}}{V_1^o}=\frac{2\delta_2}{RT}\delta_{1i}-\left(\frac{\delta_2^2}{RT}+\frac{\chi_s^{\infty}}{V_1^o}\right) \tag{12}$$

Slope is proportional to the solubility parameter of the examined material, i.e. δ_2. By using different types of probe solutes it is possible to obtain the dispersive and specific component of the solubility parameter.[23,24] It was earlier shown that solubility parameter (and its increments) could be successfully used for the characterisation of the organic layer bonded to the silica surface.[25,26]

Materials and Methods

Silica gel (Fluka, Silica gel 60, 0.2-0.5mm (35-70 mesh)) was modified in CCl_4 solution at three temperatures: room temperature (~20°C), 50°C and 70°C by the following titanium:

KR TTS - tris(isooctadecanoato-O)(2-propanolato) titanium IV, KR 7 - (isooctadecanoato-O)bis(2-methyl-2-propenoato-O)(2-propanolato) titanium IV, KR 33DS - [2-[2-(methoxy-O)ethoxy-O]ethanolato-O]tris(2-methyl-2-propenoato-O) titanium IV, KR 9S - tris(dodecylbenzenesulfonato-O)(2-propanolato) titanium IV, KR 26S - (4-aminobenzenesulfonato-O)bis(dodecylbenzenesulfonato-O)(2-propanolato) titanium IV and four zirconium {(neoalkoxy) tris(dodecylbenzenesulfonato-O) zirconiumIV - NZ09;

(neoalkoxy) tris(2-methyl-2-propenoato-O) zirconiumIV - NZ33; (neoalkoxy) tris(2-propenoato-O) zirconium IV - NZ39; (neoalkoxy) tris(2-ethyldiamino)ethylato-O) zirconiumIV - NZ44} coupling agents. All coupling agents were supplied by Kenrich Petrochemicals Inc. (USA). The modification process was carried out for 2 hours. All the modifiers (as delivered by the manufacturer) were used in 20:100 proportion to silica gel. After modification the adsorbed excess of the modifier was extracted with CCl_4 in a Soxhlet apparatus.

The inverse gas chromatography experiments were carried out under the following conditions: column stainless steel, 1 m × 3 mm I.D., measurement temperatures 120, 130 and 140°C, temperatures of the FID detector and injector 160°C; carrier gas helium, at a flow rate of 40 ml min^{-1}, Chrom 5 gas chromatograph (Kovo, Czech Republic). n-Alkanes from n-pentane to n-nonane, as well as benzene, carbon tetrachloride, chloroform and methylene chloride were chosen, as the test compounds. The amount of the injected compounds was from 0.1 to 1.0 μl of vapours to achieve the region of infinite dilution.

The values of $C' \times P_{DS}$ were calculated according to the approach proposed by Dong, Brendle and Donnet.[27] According to them

$$RT \cdot \ln V_N + C = C' \cdot P_{DS} \cdot P_{DP} - \Delta G^s \qquad (13)$$

where C and C' are constants, P_{DS} and P_{DP} are the molar deformation polarisation of the probe and solid, respectively.

For n-alkanes (where $\Delta G^s = 0$)

$$RT \cdot \ln V_N + C = C' \cdot P_{DS} \cdot P_{DP} \qquad (14)$$

Dong et al. proved that $RT \ln V_N$ is proportional to P_{DP}. This dependence is linear and the slope of the line is equal to $C'P_{DS}$. Here parameter $C'P_{DS}$ is a measure of the ability of a surface being characterised to undergo dispersive interactions.

Other solubility and surface parameters were calculated according to the respective equations presented in **Introduction**.

Results

Inverse gas chromatography method has been used in the examination of the different series of modified materials including modified fillers and systems containing modified fillers. These were: i) silica and silica gel probes were modified with the titanium, zirconium or silanes coupling agents; ii) raw and modified silicates.

The physicochemical properties of the layer formed onto the silica surface and its influence on the modified silica gel properties may be characterised by inverse gas chromatography

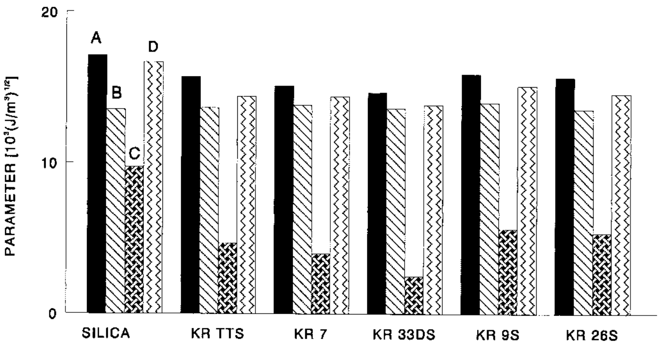

Figure 1. Influence of silica gel modification (with titanium compounds) on the values of the solubility parameter and its increments (modification temp. - 50°C; IGC temp. 120°C); A - δ_2, B - δ_d, C - δ_s, D - δ_T.

(IGC). Solubility parameter and its components were used to characterise the formed modifier layer while dispersive component of surface free energy and specific interaction parameters characterise the properties of the modified surface.[26] The influence of the modifier structure on surface parameters was found to be substantial. The type of "central atom" (titanium, zirconium or silicon, the character of modifier chains, the conditions of the modification process influenced the properties of the final product (Figure 1). Solubility parameters of the structured layer onto silica surface and the surface (both dispersive and specific) were found to be sensitive enough to the to reflect changes of the monolayer character caused by a different structure of the titanium, zirconium, silicon compounds used as the modifiers and the modification temperature. It was shown that the ability of the modified surface to the dispersive interactions (expressed by $C' \times P_{DS}$ increases with the increase of the values of the dispersive component of solubility parameter δ_T (Figure 2).

The values of surface parameters depend on the type of the central atom, the structure of organic chains of the modifier and the temperature of the modification process both for zirconium (Figure 3) and titanium (Figure 4) modified silica gel.

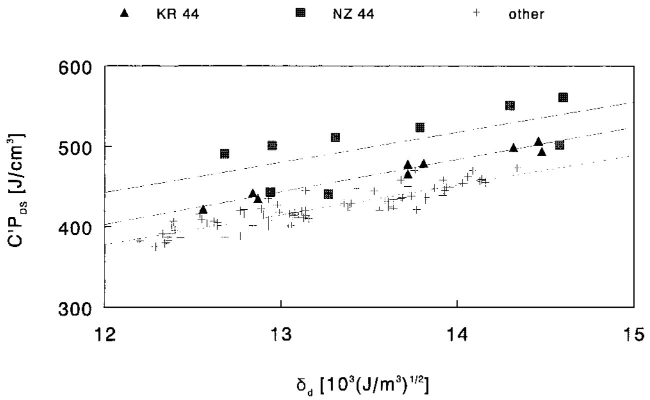

Figure 2. Relationship between the parameters $C'\times P_{DS}$ and δ_d for the silica gel modified with the titanium and zirconium coupling agents.

Dispersive properties of the examined silicates were expressed by the values of the dispersive component of surface free energy γ_s^d and Dong-Donnet parameter $C'\times P_{DS}$. γ_s^d and $C'\times P_{DS}$ values were equal to 595 [mJ/m^2] for K1 and 515 for K2 [mJ/m^2], as well as, 698

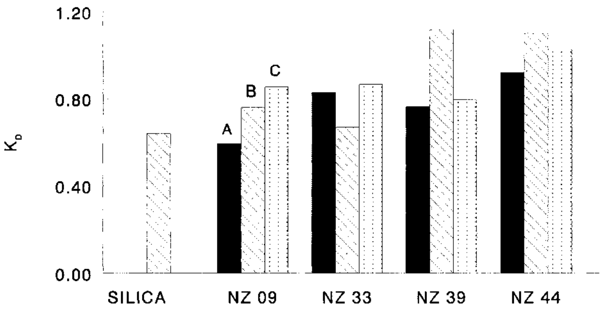

Figure 3. The influence of the silica modification on the values of K_D parameter (A - modification temp. 20°C, B – modification temp. 50°C, C – modification temp. 70°C.

[kJ/cm^3] and 571 [kJ/cm^3], respectively (at 393 K). Such high values denote highly energetic surfaces of both silicates. For talc (KT) γ_s^d was equal to 209 [mJ/m^2] and $C'\times P_{DS}$ to 414

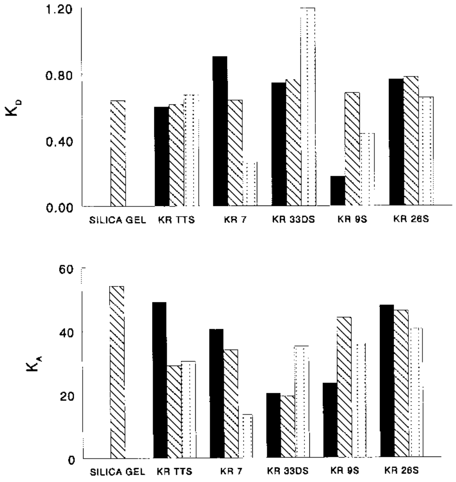

Figure 4. Surface properties of silica gel modified with titanium coupling agents (Donnet method; columns A, B and C refer to modification temperatures 20, 50 and 70°C respectively).

[kJ/cm^3] (at 363 K). Surface modification cause most often decrease of γ_s^d values, i.e. for K1 to 496 and for K2 to 482 [mJ/m^2], respectively. Similar decrease was observed in the case of $C'\times P_{DS}$ parameter. Modification of the talc surface lead to increase of both dispersive parameters; γ_s^d changed from 209 to 264 [mJ/m^2] and $C'\times P_{DS}$ from 413 to 466 [kJ/cm^3]. In each case, the values of the dispersive parameters changed in the following order: kaolin K2 → kaolin K1 → talc (raw and modified minerals).

IGC method was also used for the characterisation of the properties of different silicates: Korean talc (micronised) - KT, kaolin KOG (Surmin deposit, Poland) - K1, kaolin (Turoszów deposit, Poland) - K2. Acid-base characteristics for non-modified and modified silicates calculated according to Papirer's procedure are summarised in Figure 5. The prevailing tendency to act as electron acceptor was found for all the examined raw fillers. Highest value of K_A parameter was found for Kaolin K1. However, in this case relatively higher activity as electron donor (K_D) was also observed (in comparison to other two

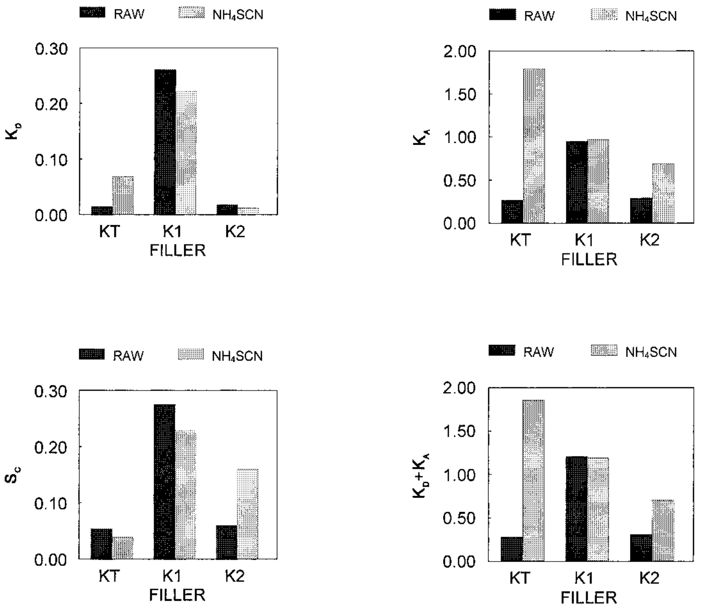

Figure 5. Surface properties of raw and modified silicates (KT - Korean micronised talc, K1 - kaolin from Surmin deposit, K2 – koalin from Turoszow deposit).

surfaces). As a result the surface of non-modified kaolin K1 exhibits relatively weak electron acceptor (acidic) character (S_C = 0.275) and relatively high surface activity as measured by (K_D+K_A) value. Both other raw minerals exhibit stronger electron acceptor character, but their surface activity was found to be small. Surface modification with the use of NH_4SCN caused increase of its electron acceptor character. The surface activity of the Korean talc (KT) significantly increased (6 times) after surface modification, of kaolin K2 increased more than two times while in the case of kaolin K1 the surface activity remained approximately on the same level.

Conclusion

The use of inverse gas chromatography allows the comparison of the effect of the modification of silica gel with silanes or zirconium or titanium modifiers. The highest values of the dispersive parameters were found for silicas modified with silanes as well as probes modified with zirconium and titanium compounds having modifier chains with polar groups at their ends (NZ44, KR44, U15, U511). Values of K_A parameter, describing electron acceptor properties, generally decreased after modification but the probes modified with zirconium compounds exhibit higher electron acceptor activity (inductive effect of zirconium atom). Values of K_D parameter, describing electron donor properties, increased after all modifications; the rate of the increase significantly depends on the type of "central" atom (Si, Zr or Ti) and the structure of modifier chain. It was also possible to distinct the different surface character (S_C values) of the probes modified with zirconium and titanium compounds. The following advantages and possibilities should be stressed: i) examination of the influence of the modifier structure on evaluated parameters and further properties of examined material (filler), ii) it is possible to examine the influence of the temperature on the modification efficiency, iii) influence of IGC experiment temperature on the values of the surface and solubility parameters; IMPORTANT: it means that we can examine our materials within the temperature range available with the use of our gas chromatograph; iv) one can examine the relationships existing between the monolayer and the surface characteristics.

Acknowledgement

This work was supported by PUT BW 32/003/2001 grant.

1. A. Voelkel, *Crit. Rev. Anal. Chem.* **1991**, *22*, 411.
2. A. Voelkel, "*Inverse gas chromatography in the examination of acid-base and some other properties of solid materials*", in: "*Adsorption on new and modified inorganic sorbents*", A.Dąbrowski, V.A.Tertykh, Eds., Elsevier Science, Amsterdam, 1996, p. 465.
3. H. P. Schreiber, D. R. Lloyd, *"Overview of Inverse Gas Chromatography"*, in: *"Inverse Gas Chromatography. Characterization of Polymers and Other Materials"*, D. R. Lloyd, T. C. Ward, H. P. Schreiber, Eds., ACS Symp. Ser. No. 391, Washington, DC, 1989, chapter 1.
4. P. Mukhopadhyay, H. P. Schreiber, *Colloids and Surfaces A* **1995**, *100*, 47.
5. S. Dong, M. Brendle, J. B. Donnet, *Chromatographia* **1989**, *28*, 469.
6. Bincai Li, *Rubber Chemistry and Technology* 69 (1996) 347.

7. A. Voelkel, J. Janas, *J. Chromatogr. A* **1993**, *65*, 141.
8. C. Saint Flour, E. Papirer, *J. Colloid Interface Sci.* **1983**, *91*, 69.
9. S. Dong, M. Brendle, J. B. Donnet, *Chromatographia* **1989**, 28, 469.
10. E. Papirer, H. Balard, A. Vidal, *Eur. Polym. J.* **1988**, *24*, 783.
11. A. Vidal, E. Papirer, Wang Meng Jiao, J.B. Donnet, *Chromatographia* **1987**, *23,* 121.
12. P. Schmitt, E. Koerper, J. Schultz, E. Papirer, *Chromatographia* **1988**, *25*, 786.
13. A. Voelkel, J. Fall, *Chromatographia* **1997**, *44*, 197.
14. N. Cordeiro, C. P. Neto, A. Gandini, M. N. Belgacem, *J. Colloid Interface Sci.* **1995**, *174*, 246.
15. H. Hadjar, H. Balard, E. Papirer, *Colloids and Surfaces A* **1995**, *103*, 111.
16. E. Morales, J. L. Acosta, *Polymer Journal* **1996**, *28*, 127.
17. V.I.Bogillo, V.P.Shkilev, A.Voelkel, *J. Mater. Chem.* **1998**, *8*, 1953.
18. V.I.Bogillo, A.Voelkel, *J.Adhesion Sci. Technol.* **1997**, *11*, 1513.
19. G. M. Dorris and D. G. Gray, *J. Colloid Interface Sci.* **1979**, *71*, 931.
20. F. L. Riddle, F. M. Fowkes, *J. Am. Chem. So.* **1990**, *112*, 3259.
21. J. H. Hildebrand, R. L. Scott, "*The Solubility of Nonelectrolytes*", Van Nostrand, Princeton, New York, 1950.
22. G. DiPaola - Baranyi, J. E. Guillet, *Macromolecules* **1978**, *11*, 228.
23. A. Voelkel, J. Janas, *J. Chromatogr. A* **1993**, *645*, 141.
24. A. Voelkel, J. Janas, *J. Fluorine Chem.* **1994**, *67*, 75.
25. W. Wasiak, A. Voelkel, I. Rykowska, *J. Chromatogr. A* **1995**, *690*, 83.
26. A. Voelkel, T. Grześkowiak, *Chromatographia* **2000**, *51*, 608.
27. S. Dong, M. Brendle, J. B. Donnet, *Chromatographia* **1989**, *28*, 469.