

CHROM. 7590

ADVANCES IN THE APPLICATION OF GAS CHROMATOGRAPHY TO THE STUDY OF HETEROGENEOUS CATALYSIS

D. S. MATHUR, U. D. CHAUBEY and A. SINHA

Planning and Development Division, Fertilizer Corporation of India Ltd., Sindri, Bihar (India)

SUMMARY

The idea of predicting the properties of solid catalysts by studying the elution behaviour of some selected solutes utilizing the “on-column catalysis” technique of gas chromatography was employed. A reduction catalyst with nickel as the active metal has been developed and the range of temperatures in which the catalyst is active has been established using carbon dioxide as the solute. *n*-Alkanes show different retention behaviour on the catalyst compared with their retention on the bare catalyst support, Chromosorb P. Their retention behaviour is explained by the mechanism of induced polarity, assuming a high charge concentration on the surface of the catalyst. A method for predicting the polarity of solid catalysts has been developed, based on the slope of the plot of partial molar free energy of adsorption against the number of methylene groups for compounds of a homologous series. A comparative study of the retention behaviour of planar, non-planar and polar molecules of C₆ hydrocarbons over the catalyst has been carried out.

INTRODUCTION

The adsorption properties and selectivity of gas–solid columns is influenced principally by the chemistry and geometry of the adsorbent surface. The chemical nature of both the adsorbent surface and the adsorbate molecules can determine the nature and energy of the interactions that occur between the molecules of the adsorbate and the adsorbent. It is simpler to predict the behaviour of molecules on homogeneous surfaces, but when the surface becomes heterogeneous as a result of coating with metal salts, the interactions become more complex. These intermolecular interactions can be expressed as the sum of physical and chemical interactions. There exist a number of energy functions, in addition to pore geometry, which may contribute to the physical interactions. The most frequently encountered functions have been discussed by Barrer and Macleod¹. During adsorption, various interactions may arise, depending on the chemical structure of the interacting molecules and the adsorbent, ranging from specific to non-specific. Non-specific adsorption always takes place between any two interacting molecules, owing mainly to dispersion forces. Specific interactions are caused by the local electron density distribution on the surfaces of the interacting molecules, which in turn means concentrations of positive or negative

charges on the periphery of individual bonds or linkages between these molecules. Molecules of *n*-alkanes are known to interact only non-specifically with all types of molecules, exhibiting mainly the universal dispersion forces related to concordant electronic motion in their molecules and not showing any electron density distribution.

It is important to stress that in the treatment of dispersion forces, energy is dependent on the polarizability of adsorbed molecules. The polarizability of complex molecules is known to be a property that is approximately additive in terms of bond contributions when the structure of the molecules can be separated into electron groups. The linear increase in the heat of adsorption of *n*-alkanes with chain length has been demonstrated by Kiselev² and others³⁻⁵. As the dispersion forces depend on the polarizability of adsorbed molecules, it is expected that gas-solid chromatographic separations of non-polar molecules can be related to the size and shape of the molecules. The specific types of intermolecular interactions arise from local electron density distributions, which in turn give rise to permanent dipole and higher multipoles in the molecules and to π -electron systems or to ions in the solid. Such specific electronic structures will react with non-polar molecules by the induced mechanism and with specific electronic structures by electron interactions.

The properties of a methanation catalyst prepared in this laboratory have been studied with respect to its retention behaviour for *n*-alkanes, alkenes and other organic compounds. The properties of the catalyst were studied in a gas chromatographic (GC) column utilizing the "on-column catalysis" technique⁶⁻¹⁰. The activity and polarity achieved by the catalyst as a function of temperature plays an important role in the retention of non-specific molecules of *n*-alkanes, and a preliminary approach towards the concept of polarity of solid adsorbents has been put forward.

EXPERIMENTAL

Chromosorb P obtained from Applied Science Labs., State College, Pa., U.S.A., was used as the support for preparing the catalyst. It was impregnated with an aqueous solution of nickel nitrate and then dried at about 120° and heated in order to convert the nitrate into oxide. The coated material was then packed uniformly in a 5 ft. \times 1/8 in. O.D. copper column in a conventional manner. The packed column was then fitted in the oven of an Aerograph Model 550 Hy-Fi gas chromatograph. A stream of hydrogen gas was allowed to pass through the column continuously. The column was then heated to 300° in a stream of hydrogen so that the nickel oxide was reduced to nickel metal, which serves as a successful catalyst for the methanation of carbon monoxide and dioxide. These two oxides are converted quantitatively into methane at the active temperatures of the catalyst. The rate of increase of activity was shown by plots of unconverted carbon dioxide peak area and carbon dioxide converted into methane peak area *versus* the column temperature. This experiment was carried out on a Beckman GC-2A gas chromatograph equipped with a thermal conductivity detector¹¹.

The GC retention behaviour of normal and cyclic alkanes, alkenes and aromatics was studied by using an Aerograph Model 550 D Hy-Fi gas chromatograph equipped with a flame ionization detector and a Honeywell-Brown recorder fitted with a disc integrator. Ultra-pure hydrogen and nitrogen gases were used as

carrier gases, and a deoxo catalyst was used to free them from oxygen. Retention times were noted with a stop-watch accurate to 0.1 sec.

RESULTS AND DISCUSSION

The activity of the methanation catalyst was tested by utilizing carbon monoxide and dioxide as solutes, which were converted into methane at specific catalyst temperatures. Mathur and Saha¹² developed a set of columns in which the catalyst column is preceded and followed by one column, each of which is used for the separation of converted and unconverted samples. Peak areas of unconverted carbon dioxide and of carbon dioxide converted into methane were plotted against column temperature for a fixed sample size of 400 μ l of carbon dioxide (Fig. 1). It was observed that the peak area of carbon dioxide decreased while that of methane increased regularly with temperature until, at 320°, the unconverted carbon dioxide peak disappeared and methane gave the maximum peak area which represents quantitative conversion.

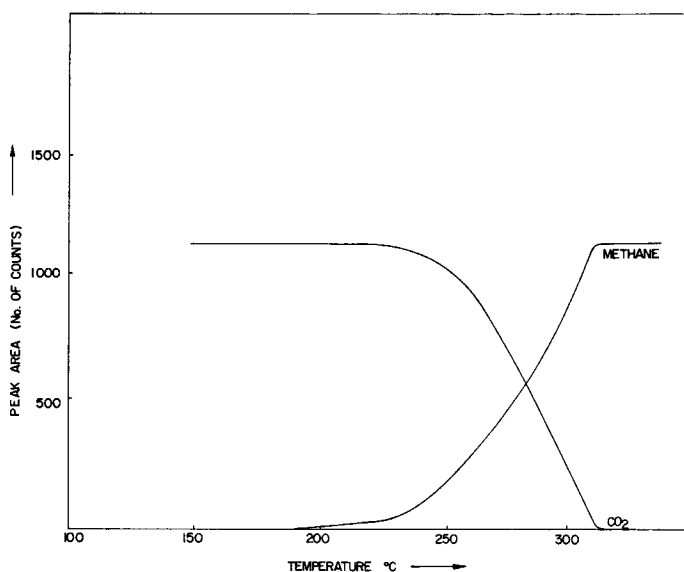


Fig. 1. Plot of peak areas *versus* column temperature.

It should be noted that the conversion of carbon dioxide takes place only when hydrogen is used as the carrier gas, because the nickel oxide that is formed as a result of decomposition of nickel nitrate reacts with the hydrogen. There are two possible reactions, one giving NiH_2 and the other NiH^+ . If it is assumed that the latter reaction predominates under the operating conditions, the catalyst should achieve polarity as a result of the reduction of nickel oxide by hydrogen. The extent of reduction of nickel oxide is therefore a function of the catalyst temperature and is maximal at 320°. It will be interesting to study the elution pattern of various normal and cyclic alkanes,

alkenes and aromatics over the catalyst column utilizing the on-column catalysis technique.

The plot of logarithm of specific retention volume against the reciprocal of the column temperature, which is rectilinear for the common GC supports, when drawn for C_5 - C_9 *n*-alkanes for this catalyst column showed very typical behaviour. *n*-Pentane and *n*-hexane gave a straight-line plot, but *n*-heptane, *n*-octane and *n*-nonane each gave two lines with different slopes that joined at about 250° in all instances (Fig. 2). It is worth mentioning that 250° is the temperature at which the conversion of carbon dioxide begins, *i.e.*, it is the temperature at which the catalyst begins to become active.

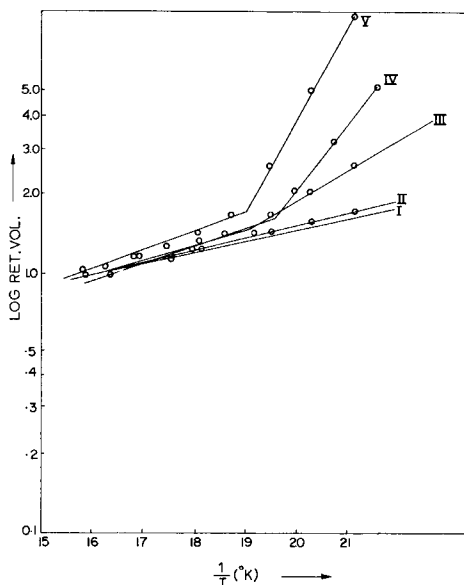


Fig. 2. Plot of specific retention volumes *versus* the reciprocal of the absolute column temperature. Solutes: I, *n*-pentane; II, *n*-hexane; III, *n*-heptane; IV, *n*-octane; V, *n*-nonane.

Induced polarity

Chromosorb P, which is utilized as the support for preparing this catalyst, loses three quarters of its surface area as a result of impregnation, so that most of the narrow pores are completely blocked and the wider pores become narrow as a result of the deposition of nickel salt on the surface. It is therefore expected that the molecular size of *n*-alkanes plays an important role in their behaviour on the catalyst. *n*-Alkane molecules are spherically symmetrical and completely non-specific in nature and are therefore not expected to be affected by the activity or polarity of the catalyst in the usual way, but it may be affected by the mechanism of induced polarity. A probable mechanism for this type of behaviour may be that the molecules of *n*-pentane and *n*-hexane are so small that they do not come close enough to the catalyst surface to be affected by induced polarity. *n*-Heptane, *n*-octane and *n*-nonane, however, show three different slopes below 250° , different from those of *n*-pentane and *n*-hexane. The

TABLE I

FREE ENERGIES OF ADSORPTION ($-\Delta G_{\text{ads.}}$) AND HEATS OF ADSORPTION ($-\Delta H_{\text{ads.}}$)
 Column: 5 ft. \times $\frac{1}{8}$ in., Chromosorb P-nickel. Carrier gas: hydrogen.

Compound	$(-\Delta G)_{\text{ads.}}$ (cal/mole)							$(-\Delta H)_{\text{ads.}}$ (kcal/mole)	
	200°	220°	240°	250°	260°	280°	300°	<250°	>250°
<i>n</i> -Pentane	412.29	369.66	318.79	295.80	279.06	249.75	117.76	1.198	1.198
<i>n</i> -Hexane	567.54	449.17	387.44	338.92	281.19	241.10	109.60	2.22	2.22
<i>n</i> -Heptane	873.78	658.41	492.95	396.37	321.96	295.33	135.27	5.22	2.658
<i>n</i> -Octane	1537.1	1088.4	717.37	474.02	392.46	338.14	191.56	11.56	2.9187
<i>n</i> -Nonane	2107.7	1546.4	917.28	570.03	504.89	351.07	188.10	16.528	3.36

larger the molecular size, the greater is the slope, and *vice versa*. Above 250°, when the catalyst becomes active and hence achieves polarity according to our previous assumptions, the slopes of the plots for these compounds change such that all three compounds give almost the same slope. This fact is clearly expressed by the heats of adsorption (Table I), which show large differences. The values of $(-\Delta H)_{\text{ads.}}$ for temperatures below 250° and those above 250° for *n*-heptane vary from 5.22 to 2.658, for *n*-octane from 11.56 to 2.92 and for *n*-nonane from 16.528 to 3.36. The values for *n*-pentane and *n*-hexane, 1.198 and 2.22, respectively, remain the same throughout the temperature range. This large variation in $(-\Delta H)_{\text{ads.}}$ values for *n*-heptane, *n*-octane and *n*-nonane at 250° may be explained on the basis that the induced polarity developed in *n*-alkane molecules increases with their molecular size. This fact is further confirmed by the adsorption energies $(-\Delta G)_{\text{ads.}}$ for *n*-C₅-C₉ compounds for temperatures in the range of 200–300°. Initially, at about 200°, when only the geometry of the catalyst plays a dominant role, these compounds are eluted according to their carbon number, but as the activity and hence the polarity of the catalyst increases, the energy of adsorption, $(-\Delta G)_{\text{ads.}}$, of *n*-nonane is comparatively more affected than that of *n*-octane, which is in turn more affected than that of *n*-heptane, as a result of which the three compounds are eluted almost together. A probable mechanism may be that the larger the size of molecules, the larger will be the number of charges it will be facing on the catalyst surface, and *vice versa*. Therefore, the size of the molecules may be directly proportional to the induced polarity developed. The polarizability data (Table II) obtained from Kiselev's work¹³ for these compounds, when plotted against molecular weight, give a straight line (Fig. 3), which supports the above discussion.

Polarity and retention

Novák *et al.*¹⁴ proposed a criterion for evaluating the polarity of a liquid phase in GLC. They assumed the additivity of the partial molar excess Gibbs free energies, ΔG , of individual groups in the molecule, and proposed the $\Delta G(\text{CH}_2)$ value as a universal criterion of the polarity of liquid phases. Further, they observed a linear relationship between ΔG and the number of methylene groups for several homologues in a homologous series. It was shown that the slope of this plot remains almost constant with temperature, while the lines shift only upwards or downwards. Their work

TABLE II
MOLECULAR WEIGHTS, POLARIZABILITIES AND BOILING POINTS OF C₅-C₉ *n*-ALKANES AND BENZENE

Compound	Mol. wt.	Polarizability (cm ² × 10 ²⁴)	Boiling point (°C)
<i>n</i> -Pentane	72.1	9.95	36.2
<i>n</i> -Hexane	86.17	11.78	69.0
<i>n</i> -Heptane	100.2	13.61	98.52
<i>n</i> -Octane	114.23	15.45*	125.8
<i>n</i> -Nonane	128.25	17.30*	150.72
Benzene	78.1	10.32	80.0

* Extrapolated values.

is obviously limited to GLC. Although they evaluated the values of $\Delta G(\text{CH}_2)$ for Porapak P and T and found it in accordance with their polarities, they did not find it feasible to evaluate the polarities of solid adsorbents.

In the present work, partial molar Gibbs free energies of adsorption, $(\Delta G)_{\text{ads.}}$, were plotted against the number of methylene groups for C₅-C₉ *n*-alkanes, and a straight line was obtained for all of the hydrocarbons. As the temperature of the catalyst is varied, the polarity of the solid changes, and hence the slope of the plot of ΔG against the number of methylene groups also changes. When the values are plotted for temperatures of 240–340°, the slope of the straight line continues to decrease until, at 320°, it becomes almost constant (Fig. 4). Incidentally, 320° is the temperature

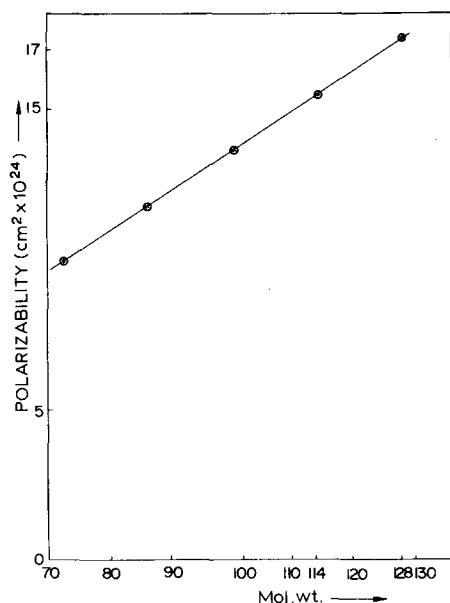


Fig. 3. Plot of polarizability versus molecular weight.

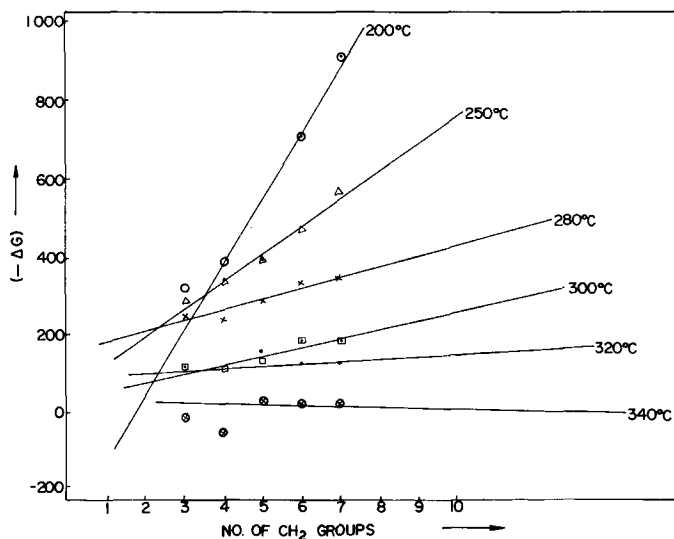


Fig. 4. Plot of $-\Delta G$ versus number of methylene groups.

for optimum activity of the catalyst. The slope of this plot therefore provides a criterion for evaluating the polarity of solids. A scale of relative polarity of adsorbents can thus be developed, selecting initially adsorbents with the maximum degree of non-polarity and maximum degree of polarity to be put at the two extremities of the scale and given the arbitrary values 0 and 100. The scale can be divided into 100 equal parts and the polarity of any unknown adsorbent can be predicted by relating it to this scale. This simple and rapid method for the evaluation of the polarity of solid adsorbents can be very useful in predicting the polarity of solid catalysts.

Specific interactions

Comparison of retention volumes and relative retention volumes with respect to those of a standard substance provide an insight into the functional dependence of non-specific interactions on the adsorbent. Table III summarizes the specific

TABLE III

SPECIFIC RETENTION VOLUMES (V_g) AND RELATIVE RETENTION VOLUMES (RV_g) ON CHROMOSORB P-NICKEL CATALYST

Column dimensions: 5 ft. \times $\frac{1}{8}$ in. Carrier gas: hydrogen.

Compound	200°		240°		280°		300°	
	V_g	RV_g	V_g	RV_g	V_g	RV_g	V_g	RV_g
<i>n</i> -Hexane	1.8285	1.0000	1.4619	1.0000	1.2455	1.0000	1.1007	1.0000
<i>n</i> -Heptane	2.5309	1.3849	1.6208	1.1086	1.3080	1.0505	1.1257	1.0218
2-Hexene	1.8643	1.0198	1.4332	0.98017	1.2631	1.0144	1.1529	1.0457
Cyclohexene	2.0877	1.1429	—	—	1.6516	1.3255	1.3586	1.2352
Benzene	2.2424	1.1989	—	—	1.6222	1.3017	1.4843	1.3490

retention volumes and relative retention volumes of various C₆ hydrocarbons with different geometries with respect to *n*-hexane for temperatures of 200, 240, 280 and 300°. The relative retention volume of 2-hexene increases regularly from 240 to 300°, indicating an increase in the relative interaction with the π -electron system as the temperature increases.

It should be noted that the catalyst achieves specificity with increase in temperature. Initially, at about 200°, when the catalyst is not active and only geometry is responsible for the retention of compounds, 2-hexene is eluted earlier than *n*-hexane, but as the catalyst becomes active, 2-hexene is held longer than *n*-hexane and this difference continues to increase with an increase in column temperature. At 300°, 2-hexene is retained for longer than even *n*-heptane. It has been shown by Hargrove and Sawyer¹⁵ that similar non-specific interactions take place with cyclohexene and benzene, but they differ in their specific interactions. The magnitude of the interactions also depends upon the closeness of approach of carbon atoms to the surface. Cyclohexene, being a non-planar molecule, can allow only four carbon atoms to approach the surface at a time, while benzene, being completely planar, allows all six carbon atoms to approach the surface. The higher relative retention volume for benzene compared with cyclohexene can thus be explained.

CONCLUSION

With a better understanding of the theory of GC, it is being more and more applied in non-analytical fields. In the present work, an attempt has been made to correlate certain aspects of catalysts and catalysis with GC parameters. After standardization of the method for determining the polarity of solid adsorbents by GC proposed in this work, by selecting a variety of adsorbents and adsorbates it will be possible to predict the polarity and acidity of solid catalysts.

ACKNOWLEDGEMENTS

The authors are grateful to Mr. K. C. Sharma, Managing Director, Fertilizer Corporation of India Ltd., and Mr. O. P. Agarwal, General Manager of the Planning and Development Division, for their constant encouragement and kind permission for this paper to be presented at the Symposium.

REFERENCES

- 1 R. M. Barrer and D. M. Macleod, *Trans. Faraday Soc.*, 51 (1955) 1290.
- 2 A. V. Kiselev, *Quart. Rev., Chem. Soc.*, 15 (1961) 99.
- 3 J. F. Hanlan and M. P. Freeman, *Can. J. Chem.*, 37 (1959) 1575.
- 4 H. W. Habgood and J. F. Hanlan, *Can. J. Chem.*, 37 (1959) 843.
- 5 R. S. Hansen, J. A. Murphy and T. C. McGee, *Trans. Faraday Soc.*, 60 (1964) 597.
- 6 J. A. Dinwiddie and W. A. Morgan, *U.S. Pat.*, 2,976,132 (1961).
- 7 E. Gil-Av and Y. M. Herzberg, *Proc. Chem. Soc.*, (1961) 316.
- 8 S. Z. Roginskii, M. I. Yanovskii and G. A. Gaziev, *Dokl. Akad. Nauk. SSSR*, 140 (1961) 1125.
- 9 E. M. Magee, *Ind. Eng. Chem., Fundam.*, 2 (1963) 32.
- 10 N. C. Saha and D. S. Mathur, *J. Chromatogr.*, 81 (1973) 207.
- 11 D. S. Mathur and N. C. Saha, *60th Session of the Indian Science Congress, Jan. 3-9, 1973, Chandigarh, India.*

- 12 D. S. Mathur and N. C. Saha, *Technology*, 11, No. 1 (1974) in press.
- 13 A. V. Kiselev, in A. Goldup (Editor), *Gas Chromatography 1964*, Institute of Petroleum, London, 1965, p. 238.
- 14 J. Novák, J. Ruzickova, S. Wičar and J. Janák, *8th International Symposium on Advances in Chromatography 1973, April 16–19th, 1973, Toronto, Canada*.
- 15 G. L. Hargrove and D. T. Sawyer, *Anal. Chem.*, 40 (1968) 409.