STUDIES ON CATALYSTS AND CATALYSIS BY THE TECHNIQUES OF GAS CHROMATOGRAPHY

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CONTENTS

1. INTRODUCTION

The research and development (R&D) of catalysts and catalysis cannot be considered to be free from empiricism, art, trial and error and chance. Perhaps the over-riding factor is the lack of sufficiently powerful experimental tools and techniques which could be used to provide unequivocal data for arriving at unambiguous relationships between specific catalytic activity and specific solid structural characteristics in the case of heterogeneous catalysis. Only recently have the immense potentialities of the numerous techniques of gas chromatography (GC) attracted the notice of catalyst researchers, which development is evident from about 400 relevant publications (excluding the innumerable analytical applications on catalytic reactions) that have appeared during the last few years. Moreover, in recent years the spectacular progress of the petroleum industry, which is one of the most catalyst-intensive industries, can be largely attributed to the extensive application of GC techniques.

Although a relatively modern technique, GC is unique in its efficiency and its scope for opening up many new routes to information required for the investigation of catalysts and catalysis. For example, in gas–solid reactions the key to the func-

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tioning of catalysts is the study of interaction of reactant and product molecules with the solid surface, which is covered by the field of gas–solid chromatography (GSC). It may be recalled that any difference in the surface properties of solids is well reflected in one or more of the various parameters of the chromatograms when the solids are used in a GSC column.

The literature describes applications of GC techniques in almost every aspect of the R&D of catalysts. GC has been far more efficient than other instrumental techniques in its analytical power for elucidating the total composition of the feed, intermediates and products of all catalytic processes — homogeneous or heterogeneous. This knowledge is essential when following the course of a reaction or several reactions that occur simultaneously. The interaction phenomena of reactants with the catalyst surface, such as adsorption, desorption, chemisorption and the thermodynamic properties associated with them, can be determined much more elegantly by GC than by any other conventional method. In the determination of the properties of solids, such as specific and active surface areas, pore specifications, mass transfer coefficient, the nature and distribution of active sites, and surface acidity, GC techniques are very convenient, rapid and efficient. Moreover, GC methods can be applied under the operating conditions of the catalysts, which is a distinct advantage over other methods. Micro-reactor–gas chromatography (MR–GC) has not only simplified compositional studies of catalytic processes, but has also provided rapid and convenient means of obtaining various physico-chemical data, rapid evaluations and comparisons of catalyst compositions, and simultaneous determinations of the performance and activity of catalysts and of the decline in their activities. MR–GC has therefore led to drastic saving in time, efforts, materials and money in the R&D of industrial catalysts and hence has been justifiably described as a "micro pilot plant".

However, the most radical application of GC is in the simultaneous exploitation of the chromatographic separating power and the catalytic activity of porous solids. A revolution in industrial catalytic processes (gas–solid reactions) can be expected if these chromatographic reactors can be successfully scaled up.

During the last decade or so, a number of powerful instrumental techniques, such as the scanning electron microscope, the field ion microscope, lower-energy electron diffraction, electron spin resonance and nuclear magnetic resonance spectrometers, have emerged that can be used to obtain a more complete understanding of the functioning of catalysts. After GC techniques have been used to show the existence of differences in physico-chemical and catalytic activities, the solid surfaces can be examined in detail by the above instrumental techniques so as to give an eventual correlation between solid structure and catalytic activity. In addition, the study of catalysis by GC methods can be complemented, if necessary, by other powerful physical techniques.

2. OBJECTIVES

Contributions made so far represent little more than a beginning, so that the scope of GC techniques in the investigation of catalysts and catalysis is really vast. Closer collaboration between groups of researchers in the fields of catalysts, structure of solids and GC is essential for the rapid and unequivocal verification of concepts

and ideas, and hence for raising the status of the R&D of catalysts and catalysis to that of a completely reproducible science and technology. The aim of this paper is not to give a complete review of the literature, but to highlight the significant advances brought about by GC in most of the major facets of the R&D of catalysts and catalysis. The existing references are not commented upon individually, rather the important applications with further potential are tabulated under appropriate headings. A few unexplored potentialities of GC in the field of catalysts and catalysis are pointed out. Relevant work under progress in this laboratory is also discussed briefly.

3. SCOPE OF GC TECHNIQUES

The applications of GC techniques in the R&D of catalysis can be divided into two parts, namely, analytical and non-analytical. For composition studies, GC is unique in analytical chemistry with its vast array of techniques and methodology. Most analytical problems, if not all, associated with homogeneous catalytic reactions can be solved efficiently by GC.

During the last decade, much progress has been made in non-analytical applications of GC[1-4]. In studies of catalysts and catalysis, these applications include the mechanisms, kinetics and thermodynamics of chemical reactions, the characterization and properties of solid surfaces, and the interaction of gaseous molecules on solid surfaces etc. These applications have almost exclusively utilized the elution method of development of gas chromatograms, displacement and frontal methods being used only infrequently.

4. ANALYTICAL APPLICATIONS

(a) General

The lack of methods for the rapid and accurate analysis of feeds, intermediates and products has long hampered progress in the understanding of catalysis. The unique analytical power of GC, which originated from its versatility, simplicity, reliability, speed and the requirement for extremely small sample sizes, has led to the great popularity of GC techniques for determining the total composition of feeds, intermediates and products of catalysis in both research and industry. GC applications in this area are too numerous to be tabulated. GC has thus led to a drastic reduction in the use of conventional methods in the R&D of catalysts. The more complete analytical information obtained by GC provides better control and gives a correlation between catalytic processes and operating variables, leading to the desired product distribution and the simultaneous determination of kinetic expressions for all the reaction paths. Major applications of GC on reaction mechanisms and kinetics of catalytic processes are given in Table 1.

GC can lead to further reductions of effort, time and money in the R&D of industrial catalysts by coupling several gas chromatographs with a computer and by providing automatic injection of samples from research/pilot plant/production units. As the demand for more sophisticated catalytic products from more complex and exotic feeds is obviously increasing, the popularity of GC will also increase. This will apply especially to organic chemical industries, but inorganic compounds are also being studied by GC in rapidly increasing numbers.

TABLE 1

APPLICATIONS OF GC IN STUDIES OF REACTION MECHANISMS AND KINETICS
OF CATALYSIS (HETEROGENEOUS) PROCESSES

Title of paper	Reaction system	Reference
New microcatalytic chromatographic technique for studying catalytic reactions	Microcatalytic technique	5
An improved microcatalytic technique	Microcatalytic technique	6
Study of catalytic reactions by vapour-phase chromatography	Catalytic reaction	7
Versatile microcatalytic chromatographic instrument for use in the study of catalysts	Catalytic reaction	8
Use of tracers and GC in studying catalytic reactions	Reaction kinetics	9
Reactivities of naphthenes over a platinum reforming catalyst by GC technique	Reactivity of naphthenes	10
Some observations on the acid-catalyzed reaction between acid anhydrides and tertiary alcohols	Mechanism, reaction between acid anhydride and tertiary alcohols	11
Mechanism of the disproportionation of ethyltrimethylsilane	Mechanism of disproportionation	12
Theoretical basis for kinetic effects in GSC	Theoretical treatment	13
A GC study of the catalytic isomerization of cyclopropane	Isomerization of cyclopropane	14
The microcatalytic chromatographic technique and its application to commercial GC	Microcatalytic reaction	15
Acid-catalyzed methanolysis of enol acetates	Kinetics of methanolysis of enol acetates	16
Hydrolysis of 6-acylcyclohex-2-enones and the base-catalyzed rearrangement of cyclohex-2-enones	Mechanism of rearrangement of cyclohex-2-enones	17
Stereochemistry and the mechanism of hydrogenation of cycloolefins on a platinum catalyst	Mechanism of hydrogenation of cycloolefins	18
Catalytic hydrogenation of α,β-unsaturated ketones. II. Mechanism of hydrogenation in acidic medium	Mechanism of cyclohydrogenation of α,β-unsaturated ketones	19
Catalysis of metals of Group VIII. V. The kinetics of hydrogenation of cyclopropane and methylcyclopropane	Kinetics of hydrogenation of cyclopropane and methylcyclopropane	20
The catalytic isomerization of cyclopropane. Effect of residual water and the nature of exchangeable cations	Mechanism of catalytic isomerization of cyclopropane	21
Kinetics of catalytic and homogeneous chemical reaction	Kinetics of hydrogenation of linoleate	22
Microcatalytic hydrogenation and dehydrogenation combined with GLC	Hydrogenation and dehydrogenation	23

TABLE 1 (*continued*)

Title of paper	Reaction system	Reference
Study of vapour-phase chromatography of some reactions of amides derived from piperidine	Reactions of amides	24
Kinetics of the effects of nitric oxide and nitrosyl chloride on the gas-phase chlorination of chloroform	Kinetics of chlorination of nitric oxide and nitrosyl chloride	25
A study of the photochemical reaction of 2-cyclohexanones with substituted olefins	Mechanism of reaction of 2-cyclohexanones with substituted olefins	26
An attempt to study complex formation between 1,3,5-trinitrobenzene and olefins	Reaction of 1,3,5-trinitrobenzene	27
Kinetics of *n*-butane adsorption on various particle sizes of silica gel by GSC	Kinetics of adsorption of *n*-butane	28
Application of GC in studies of the kinetics of copolymerisation reactions	Kinetics of copolymerisation reactions	29
A kinetic study of the cyclohexadienyl radical. I. Disproportionation and combination with the isopropyl radical	Kinetic and mechanistic study of cyclohexadienyl radical	30
Reaction of benzoyl chloride with triphenyltin hydride	Benzoyl chloride with triphenyltin hydride	31
Kinetics of the reaction H + D₂ →HD + D	Kinetics of reaction between hydrogen and deuterium	32
Reactions of thiols with sulfoxide. II. Kinetics and mechanistic implications	Kinetics and mechanism. Reaction of thiols with sulphoxide	33
Kinetic isotope effect in the reaction of N-methylaniline and 3-chloro-1-butene	Kinetics of reaction between N-methylaniline and 3-chloro-1-butene	34
Kinetics of vapour phase hydrocarbon–ozone reactions	Kinetics. Hydrocarbon–ozone reactions	35
Kinetics of some reactions of nitrosoalkanes	Kinetics. Reactions of nitrosoalkanes	36
Nitrosation reactions of primary vinylamines. Possible divalent carbon intermediate	Mechanism. Nitrosation of primary vinylamines	37
Kinetics of catalytic dehydrogenation of ethylbenzene to styrene	Kinetics. Hydrogenation of ethylbenzene	38
Mechanism of the catalytic synthesis of picolines. Catalytic conversion of acetaldehydes on silica alumina	Mechanism. Synthesis of picolines	39
The alcoholysis of trialkylalkoxysilanes. Part I. A kinetic study of the methanolysis of methyl 2,3,4,6-tetra-O-trimethylsilyl-α-D-glucopyranoside	Kinetics and mechanism. Methanolysis of methyl 2,3,4,6-tetra-O-trimethylsilyl-α-D-glucopyranoside	40
Kinetics of the homogeneous partial oxidation of o-xylene vapour by air	Kinetics. Oxidation of o-xylene	41
Pulse method for the investigation of the velocity of heterogeneous solid phase–gas reactions combined with GC analysis of reaction products	Kinetics. Heterogeneous gas reactions	42

TABLE 1 (*continued*)

Title of paper	Reaction system	Reference
A chromatographic method for studying the kinetics of chemical reaction in the stationary phase	Kinetics of reaction in stationary phase	43
Differential chromatographic method of studying the kinetics of chemical reactions	Kinetics of chemical reaction	44
Reaction kinetics as a diagnosis tool for the GC column	Kinetics. A reverse technique	45
GC methods for studying the kinetics of liquid-phase reactions	Kinetics. Liquid-phase reactions	46
Chemisorption rates by chromatography	Kinetics. Chemisorption	47
Theoretical basis for study of the equilibrium and kinetics of adsorption processes by GC	Theoretical treatment	48
Analysis of intermediate products of the catalytic reduction of chloro- and dichloronitrobenzenes	Reduction of chloro- and dichloronitro-benzene	49

(b) Trace analysis of catalyst poisons

GC techniques are also useful in monitoring trace compounds that cause a decrease in the activity of and also cause poisoning of catalysts. GC methodology is already known for the trace determination of moisture, oxygen, nitrogen and sulphur compounds, etc. The use of selective and structure-specific detectors, such as microcoulometric, flame photometric, electron capture and thermionic detectors, has considerably reduced detectable limits to nanogram and picogram levels. In the determination of oxides of carbon, the sensitivity of the katharometer can be augmented 1000-fold or more by methanation and the application of a flame ionization detector. In this laboratory[50], an efficient catalyst has been developed for the complete and almost instantaneous conversion of the oxides of carbon to methane. The column technology and operating conditions have been standardized for determining these compounds in the presence of light hydrocarbons and gases.

(c) Deposits on catalysts

GC can also be used to establish the nature of the so-called coke deposits on catalysts during use. Karmakar[51] extracted carbonaceous compounds deposited on a cracking catalyst with acetone and found a significant difference in the gas chromatograms of *n*-pentane and isopentane which had been subjected separately to cracking under identical conditions.

GC techniques can be used not only to compare the coke-deposit properties of different feed molecules, but also to aid in devising remedial steps.

5. PHYSICO-CHEMICAL PROPERTIES OF SOLID SURFACES

(a) Adsorption isotherms and associated thermodynamic properties

A number of properties of the geometry and chemistry of pore surfaces are associated with the catalytic properties of solids. Changes in these properties will

affect the interaction of sorbate molecules with the solid surface and hence will be reflected in one or more of the sensitive parameters of GSC peaks. GSC techniques are therefore particularly suitable for determining the properties of catalyst surfaces even under the conditions that are required for catalytic reactions. Kiselev[52] has investigated the nature of sorbate–sorbent interactions and has classified adsorbates into four types and adsorbents into three types from considerations of electron-density distributions that cause differences in adsorption isotherms. The pore surface is perhaps most elaborately characterized by the adsorption isotherms. Brunauer, Emmett and Teller[53] mentioned five types of adsorption isotherms, all of which were determined by Gregg and Stock[54] by the elution GSC technique of Glueckauf[55]. Kobayashi, Chappelear and Deans[3] reviewed GSC methods used during the period 1952–1967 for the determination of adsorption isotherms. In 1971, Choudhary and Doraiswamy[56] made an exhaustive review of GSC methods for the determination not only of adsorption–desorption isotherms, isobars and isosteres, but also the associated properties including heat of adsorption, nature of adsorption and adsorption–desorption kinetics. The GSC methods used include the elution (which is the most common), frontal and displacement modes of operation upon solid surfaces of both conventional adsorbents, supports and catalysts. The recent development of many ultra-sensitive GC detectors has widened the scope of low pressure adsorption studies in the linear reversible region of adsorption and also for solids of very low adsorption capacity. In the high pressure region, up to 2000 p.s.i.a. has been used. A distinct advantage of GSC methods is their applicability to high adsorption temperatures, when the slow static methods with long contact times may cause thermal decomposition of the adsorbates. An important advantage of using adsorption isotherms is that many thermodynamic properties relevant to catalysis can be conveniently, reliably and rapidly derived from them. GC methods for the determination of adsorption isotherms and associated thermodynamic properties are given in Table 2. The retention volume in GSC is closely related to the adsorption phenomenon and is, therefore, a source of information on gas–solid interaction potentials. Hansen *et al.*[90] extended the mathematical treatment of this subject together with experimental verification with inert gases and light hydrocarbons.

(b) Specific surface area

Nelson and Eggertsen[120] demonstrated successfully that the surface area of a solid can be determined by GC much more conveniently and rapidly than by the classical BET method. This dynamic and continuous flow method was applied with little modification by a number of workers (see Table 3, pp. 218, 219). A commercial gas chromatograph has been developed by Ettre and Brenner[121] for the determination of both adsorption isotherms and surface area. Kuge and Yoshikawa[122] directly determined the amount of adsorbate for monolayer coverage from the changes in peak shape with sample size. However, the most radical refinement in recent years involves the use of organic compounds as adsorbates. The resultant major advantages include: choice of carrier gas other than helium; elimination of the mandatory and tedious BET procedures of prior sample de-gassing and use of cryogenic temperatures; and application of ultrasensitive detectors besides thermal conductivity detectors for the determination of very low surface area with better precision. Recently, Ghosh, Sarkar and Saha[123] have recommended the use of spherically symmetrical and non-reactive

TABLE 2

GC APPLICATIONS IN THE DETERMINATION OF ADSORPTION ISOTHERMS AND
THERMODYNAMIC DATA ON SOLID CATALYSTS

Title of paper	System studied	Reference
Saturation and performance of ion-exchange and adsorption columns	Mathematical treatment under the condition of non-linear adsorption isotherm	57
The mathematics of exchange processes in fixed columns. I. Mathematical solutions and asymptotic expansions	Rate of mass transfer with non-linear adsorption isotherm	58
—	Carbon dioxide adsorption on activated carbon. Different heats of adsorption studied	59
The chromatography of gases and vapours. III. Determination of adsorption isotherms	Adsorption isotherms of cyclohexane and benzene on carbon	60
The interaction of rare gases atoms with surfaces	Basic theory on interaction potential and its relation with GC	61
The interaction of gas molecules with capillary and crystal lattice surfaces	Fundamental experiments on the interaction potential and its relation with GC parameters	62
Longitudinal diffusion and resistance to mass transfer as causes of non-ideality in chromatography	Mathematical treatment of gas–liquid mass transfer term	63
Determination of adsorption isotherms by vapour-phase chromatography	Adsorption isotherms of carbon dioxide and acetylene and their mixture determined by frontal chromatography	64
The determination of heats of adsorption by GSC	Heat of adsorption of some low-boiling gases and light hydrocarbons	65
Sorption isotherms and chromatographic behaviour of vapours	Adsorption isotherm from elution chromatograms	54
Gas adsorption chromatography	A theoretical connection between static measurements and gas adsorption chromatography	66
A GC study of the adsorptive properties of a series of activated charcoals	Adsorptive properties of nitrogen and simpler hydrocarbons on a steam activated charcoal	67
The virial treatment of the interaction of gas molecules with solid surfaces	Variation of interaction potential with temperature	68
Testing of adsorbents and catalysts by GC	GC properties of adsorbents and catalysts	69
Testing of adsorbents and catalysts by GC. I. Determination of the relative surface of adsorbents from values established by GC	Derivation of a relation between retention volume and heat of adsorption	70
Sorption and diffusion of simple paraffins in silica–alumina cracking catalysts	Paraffins on silica–alumina catalyst	71
Potential energy barrier for rotation and condensation coefficient of hydrogen and deuterium on alumina by GC	Potential energy barrier hindering rotation and the striking coefficient of hydrogen and deuterium molecules on alumina	72

TABLE 2 (*continued*)

Title of paper	System studied	Reference
Determination of heat of adsorption by elution chromatography	Heat of adsorption of carbon dioxide on activated charcoal	73
—	Measurement of adsorption isotherms	74
A comparison of the measurement of heats of adsorption by calorimetric and chromatographic methods on the system nitrogen–bone mineral	Heat of adsorption of nitrogen	75
Measurement of adsorption isotherms and surface areas by continuous flow method	Adsorption of benzene, *n*-hexane on molecular sieve 13 ×, silica gel, calcined alumina and platinized alumina	76
Microdetection of adsorption isotherms by GC	Adsorption of carbon dioxide on activated charcoal	77
Mathematics of adsorption for pulse flow through packed columns	Adsorption of hydrogen on molecular sieves	78
Determination of heats of adsorption by transient response technique	Examination of various types of adsorption isotherms	79
Measurement of adsorption isotherms at high temperature with the help of gas–solid elution chromatography	Isotherms of benzene on silica gel, alumina and silica–alumina cracking catalysts and also adsorption of hexane and benzene on alumina	80
Determination of the surface and calculation of the sorption isotherms by the method of heat desorption	Critical evaluation of the methods of obtaining adsorption isotherms by previous workers	81
Investigation by GC of non-reduced iron catalysts	Heats of adsorption of propane and butane on four ferric oxide catalysts	82
High temperature adsorption studies on silica–alumina and molybdena-alumina catalysts by use of flow techniques	Adsorption of benzene and *n*-heptane on silica–alumina and molybdena–alumina catalysts	83
Adsorption and linear GSC	Heats of adsorption of hydrocarbons at temperatures below their boiling points from activated alumina	84
High temperature adsorption and determination of surface area of solids	Interaction potential and its relation to adsorption	85
Low temperature limiting behaviour of gas imperfections due to gas–solid interactions	A low temperature asymptotic expression for the first-order gas–solid interaction	86
An experimental study of adsorption chromatography with a non-linear isotherm using the system isobutylene–activated alumina	Adsorption characteristics of isobutylene-activated alumina	87
—	Heats of adsorption of carbon monoxide on doped nickel oxide	88
—	Retention volumes and k values determined for ethane, propane and *n*-butane on silica gel	89
GC measurement of gas–solid interaction potential and solid surface areas	Dependence of retention volumes of argon, nitrogen, carbon monoxide, methane, ethane, ethylene, propane and propylene on temperature from activated carbon	90

TABLE 2 (*continued*)

Title of paper	System studied	Reference
—	Adsorption studies of various gases with a Columbia L activated charcoal surface	91
GC determinations of the absolute values of the retention volumes and the heat of adsorption of hydrocarbons on silica gels of different structures	Heats of adsorption of hydrocarbons, methane through *n*-decane, on silica gel	92
GC determination of energy of hydrogen bonds in the adsorbed layers of alcohols on graphitized carbon black	Heats of adsorption of *n*-paraffins and *n*-alcohols, energy of hydrogen bonds	93
The study of gas–solid equilibrium at high pressures by GC. I. Ethane, propane and butane at essentially infinite dilutions in methane–silica gel system	Slope values of isotherms for ethane, propane and *n*-butane on silica gel	94
—	Discussion of various kinds of inter-molecular interactions involved in GC	95
Determination of entropies of adsorption by GC	Adsorption isotherms of benzene on silica gel	96
Multicomponent gas–solid equilibrium at high pressures by GC. II. Generalization of the theory and application to the methane–propane–silica gel system	General relationship for the determination of total and component adsorption	97
Measurement of adsorption isotherms by GC technique	Discussion of the use of peak maxima compared with the single injection technique for calculating adsorption isotherms	98
Determining adsorption heats of hydrocarbons on zeolites by GC	Determination of the differential heats of adsorption for oxygen, nitrogen and various light hydrocarbons on zeolites	99
The determination of the heats of adsorption by the GC method	Estimation of heats of adsorption of low-boiling hydrocarbons and inorganic gases on activated charcoal, alumina, silica gel and synthetic zeolites	100
—	Adsorption isotherms of organic vapours on graphitized carbon black	101
—	Adsorption isotherms for benzene, *n*-hexane and cyclohexane on alumina	102
Isotherms of adsorption and rapid determination of the specific surface area by GC method of thermal desorption	Adsorption isotherms of non-porous and coarsely porous adsorbents	103
Investigation of magnesium oxide surface by adsorption and GC methods	Adsorption characteristics of magnesium oxide	104
Testing of adsorbents and catalysts by means of GC	Evaluation of adsorbents and catalysts	105
Gas adsorption	General	106
—	Heats of adsorption for various polar and non-polar organic molecules over chloride salts of alkali metals	107

TABLE 2 (*continued*)

Title of paper	System studied	Reference
Determination of entropies of adsorption by GC	Determination of heats of adsorption utilizing temperature dependence of retention volume	108
The possibility of the determination of adsorption potential. Distribution on adsorbent surface by GC	Adsorption potential of carbon disulphide on silica gel	109
Adsorption isotherms and heats of adsorption by frontal analysis chromatography	Measurement of adsorption isotherm of nitrogen, air, oxygen and carbon monoxide on carbon black and bone mineral	110
Measurement of phase equilibria at high pressures by tracer pulse chromatography	Apparatus to measure adsorption equilibrium isotherms	111
GC determination of non-linear adsorption isotherms at low concentrations	Determination of non-linear isotherm for a polar solute	112
Adsorption of polar compounds on amorphous boron	Heats of adsorption of water, methanol, acetone, ammonia and trimethylamine on amorphous boron as adsorbent	113
Measurement of adsorption isotherms by GC technique	General adsorption isotherm	114
Determination of heats of adsorption and identification under conditions of non-linear temperature programmed chromatography	Heats of adsorption of ethylene oxide, benzene and alkanes from pentane to octane on channel black	115
GC determination of reversible adsorption of hydrogen. VIII. Reversible adsorption of hydrogen over cobalt oxide	Adsorption of hydrogen over cobalt oxide	116
GC study of hydrogen adsorption on supported metals	Adsorption of hydrogen on supported metals	117
Study of the chemisorption properties of zinc oxide based catalyst by GC	Chemisorption properties of catalysts	118
Determination of Henry's law constants, enthalpies and potential energies of adsorption, and surface area by GSC	Adsorption of inert gases, nitrogen and methane on active carbon	119

normal paraffins as adsorbates, which have the least possibility of being retained on solids by forces other than adsorption and hence have the maximum possibility of giving the total surface area. These workers also established a linear relation between the logarithm of surface area and the slope determined from the plot of retention data against the number of carbon atoms of a selected group of normal paraffins. By constructing such a calibration curve, the surface areas of solids can be compared and evaluated very rapidly.

GC methods for the determination of surface area are given in Table 3. References 81, 87, 92, 105 and 111, listed in Table 2, also deal with the surface area of solids.

(c) *Nature of pores and pore size distribution*

The nature of pores, particularly the pore volume, average pore opening, distribution of pore size and surface area among the various pore sizes, etc., all play

TABLE 3

EXAMPLES OF THE GC DETERMINATION OF SURFACE AREA OF CATALYSTS, SUPPORTS AND ACTIVE SITES

Title of paper	System studied	Reference
Contribution to the relation between the characteristic retention volume and adsorbent surface area in GSC	Adsorbent surface area	124
Testing of adsorbents and catalysts by GC	Surface area of MgO on activated carbon	69
Physico-chemical measurements by GC	Identification of types of adsorption	125
An adsorption flow method for specific metal surface area determination	Specific metal surface area of multicomponent catalysts by CO chemisorption	126
Flow adsorption method for catalyst metal surface measurements	CO chemisorption on platinum, nickel and rhodium catalysts	127
Application of GC in studies of the chemisorption of hydrogen on metal surfaces	Hydrogen chemisorption on activated Pt powder	128
Adsorption measurements during surface catalysis	General development	129
Investigation of magnesium oxide surface by adsorption and GC methods	MgO surface by adsorption of benzene	104
A new method to determine relative surface area by GC	Dipyridine copper nitrate surface by adsorption of benzene, cyclohexane and n-hexane	122
Isotherm of adsorption and rapid determination of the specific surface area by GC method of thermal desorption	Adsorption and thermal desorption isotherms	103
GC determination of the surface area of solid materials	n-Hexane, n-heptane and n-octane on CuO, ZnO, $Zn(OH)_2$, $Zn(CO_3)$, $Ca(OH)_2$, etc.	130
Determination of very small surfaces of powdery substances by the heat of desorption method	Surface area of low surface area substances using organic vapours	131
Pore-size distribution by a rapid continuous flow method	N_2 desorption on SiO_2–Al_2O_3 catalyst	132
Gas phase chromatographic apparatus used to study the surface properties of solids	N_2 adsorption on nickel	133
Comparison of various chromatographic techniques for determining the specific surfaces of solids from argon adsorption	General, applied to various systems	134
Chromatographic methods for studying solid catalysts	General	135
Differential chromatographic determination of complex catalyst surfaces. I. Nickel on supports	Chemisorption of oxygen on nickel	136
Application of GSC to the measurement of small metallic surface areas of bulk specimens	Methane adsorbed on iron	137

TABLE 3 (*continued*)

Title of paper	System studied	Reference
Chromatographic measurements of hydrogen adsorption on supported metal catalysts	Hydrogen adsorption on Pt and Ni catalysts	138
Chemisorption of carbon monoxide on metal surfaces by pulse chromatography	CO chemisorption on Ni catalysts	139
Apparatus for evaluation of pore-size distribution	N$_2$ adsorption at liquid nitrogen temperature	140

an important role in the catalytic behaviour of porous solids. The classical pressure–volume methods for the determination of these properties of pores are increasingly being superseded by the dynamic, convenient and rapid GC methods. The principle of these GC methods is to equilibrate the solid sample (previously outgassed and maintained at the temperature of liquid nitrogen) with a nitrogen–helium mixture of varying relative pressures of nitrogen (assuming that helium is not appreciably adsorbed), and calculating the pore size distribution from the adsorption or desorption isotherms by conventional mathematics[141–145].

In one such group of methods, represented in the paper of Winter[140], the relative pressure of nitrogen over the sample was varied by changing the percentage of nitrogen in its mixture with helium, but keeping the total equilibrium pressure constant at about 1 atm. The increased adsorption of nitrogen corresponding to an increase in the relative pressure is calculated from the area under the GC peak, monitored by a thermal conductivity cell, whose reference and sensing sides are both maintained at atmospheric pressure at a constant flow-rate. The main drawback of such methods is the non-linear response of the katharometer owing to the wide variation of the composition of the mixed carrier gas. Therefore, Haley[146] varied the total pressure of the adsorbate gas mixture, but kept the proportion of nitrogen constant at 10% to correspond to relative nitrogen pressures of 0.16 to 1.00. Using pressure regulators, Haley maintained a constant carrier pressure in both halves of the katharometer and claimed that a better detector performance was obtained. While Haley preferred the adsorption branch of the isotherm, Cahen et al.[147] used the desorption part by decreasing the total gas pressure steadily and continuously over the sample. The authors of this review[148] are working on a different method for the determination of pore-size distribution. It has been observed that the retention volume of methane is contributed to only by the pores of radius below around 40 Å and that of ethane by those below around 70 Å, and so on. Hence, by using a series of normal paraffins as adsorbates, the pore-size distribution can be determined more rapidly and precisely, because the use of cryogenic temperatures and prior de-gassing of samples are rendered unnecessary, and the thermal conductivity detector can be replaced by ultra-sensitive ionization detectors.

(d) *Surface area of active metal sites*

GC techniques have been used for the determination of the surface area, nature, number, distribution and degree of dispersion of active metal sites in multi-component

catalysts. The important applications have been given in Table 3. The various principles applied for the GSC determination of active metal surface area can be summarised as: (*i*) repetitive injections of a chemisorbed species in the carrier gas stream of a GSC column, packed with the catalyst under test, until a column breakthrough is attained; (*ii*) by injecting a strongly polar compound in order to displace quantitatively the solute that has already saturated the bulk of the catalyst by chemisorption; (*iii*) by introducing a reagent that reacts quantitatively with the chemisorbed species to generate volatile products that are monitored by the GC detector; (*iv*) by completely desorbing the chemisorbed species (which sometimes undergo chemical transformation) after subjecting them to high temperatures; and (*v*) by simultaneous determination of the activity of a catalyst that is deactivated in steps by injecting known amounts of a catalyst-poisoning substance until the activity of the catalyst becomes zero. Hydrogen, carbon monoxide, ethylene and cyclopropane have so far been used as chemisorbed compounds. After the amounts of these chemisorbates are determined by GC, their stoichiometric ratio with the active metal should be independently checked by spectroscopic and other methods for reliable calculation of results.

There is considerable scope for the refinement of the above methods as well as for applying new approaches. After a metal-coated catalyst has been treated with a chemisorbate, it behaves as a GLC support. Then, by using a specific solute, whose retention is completely or predominantly (in which case a blank determination will be necessary with the bare support upon which the metal has been coated) controlled by the active metal, the active surface area can be calculated from the retention volume of the specific solute. Work on this aspect is under progress in the laboratory of the authors of this review.

(e) Miscellaneous properties

The gas–solid mass-transfer coefficient term in the HETP (height equivalent to a theoretical plate) theory of GSC is a very useful parameter for the in-depth investigation of the interactions of gaseous molecules on solid surfaces. Habgood and Hanlan[67] have developed this mass-transfer term of the original Van Deemter equation mathematically to include several parameters, such as the particle diameter, support permeability, distribution coefficient and effective diffusivity. As the experimental methods for the determination of HETP and the isolation of the mass-transfer term are well developed in GSC, the above parameters can be determined more conveniently by GC. In fact, the effective diffusivities of catalysts packed in GSC columns have been measured by several workers[149-153] by the pulsed-flow GC technique and the results were found to be in good agreement with conventional steady-state methods.

Starting with the vastly improved GSC theory of Kubin[154,155] and Kucera[156], Schneider and Smith[157,158] gave an elaborate mathematical treatment of the phenomena of adsorption and diffusion of gases on porous solids. These workers applied a set of differential equations for the experimental determination of axial dispersion coefficient, intraparticle diffusion coefficient, surface diffusion coefficient at very low surface coverage, adsorption rate constant, mass-transfer coefficient and adsorption equilibrium constants by the technique of GSC.

During the last few years, various GC methods have been applied to the study

of the properties of active sites. These methods for the investigation of the acidity and basicity of active sites and their relative strengths, numbers and distribution on catalysts have been reviewed by Choudhary and Doraiswamy[56].

6. PREDICTION OF CATALYTIC EFFECT

Certain potentialities of GSC for the investigation of the basic catalytic properties of solids still remain unexplored. For example, no correlation is known between the changes that occur in the physics and chemistry of pore surface, particularly around the active sites, under conditions in the neighbourhood of catalytic reaction, and the changes in the retention properties of a reactant, when the same solid catalyst is packed into a GSC column for such an investigation. GC techniques have several advantages over conventional methods, such as its applicability over a wide range of temperature and pressure and its sensitivity to any changes (on the surface of the catalyst) that cause corresponding changes in the sorbate–sorbent interaction energy.

The experimental technique for such an application can be illustrated with a solid catalyst, where the active catalytic principle is a metal distributed on a porous adsorbent. By using two identical columns, one packed with the blank support and the other with the supported catalyst, the changes in retention properties of both the reactant and non-reactant molecules can be measured in a dual-column gas chromatograph under various conditions of temperature, pressure, space velocity, etc. GSC changes can be expected in (a) adsorption isotherms and (b) one or more of the various parameters of the elution band, such as the peak symmetry, shape, tailing, half-width, HETP, gas–solid mass-transfer coefficient, relative retention and retention index (with respect to two suitable non-reacting molecules). The results can be analysed meaningfully in terms of differential changes of any retention property between the support and the catalyst columns. These differential changes represent the contribution of the active metal sites only, because the support effects have been cancelled out. Graphs of the differential changes against operating variables or the extent of catalytic conversion of a reactant will illustrate the changes in various GSC properties during catalysis.

By studying several catalyst formulations, one can identify one or more specific GSC properties, which are observed only with a catalytically active solid and not with others. This will eventually lead to a reliable causal relationship between the catalytic activity and a set of GSC properties. Moreover, one can find the types of molecules upon which a solid will act catalytically. This study can be put to another important use, namely to determine the changes caused by the active metal on the surrounding environment of the support. This can be achieved by measuring the differential changes in the GSC properties of two solutes, one specific for the support only and the other for the metal component only. Work in these areas is being carried out in the laboratory of the authors of this review[148].

The differential changes mentioned above in the region of catalytic activity are most likely to be associated with the phenomenon of activated adsorption or chemisorption of a reactant. Ivanova and Zhukhovitskii[159] measured changes in the retention volume (V_R) of a reactant on a solid catalyst at various temperatures and plotted

log V_R against temperature. This graph can be more meaningfully represented by replacing V_R with

$$\Delta(RRT)=(RRT)_{catalyst}-(RRT)_{bare\ support}$$

RRT is the difference in the retention times of a reactant and a solute that is not retained either on the support or on the supported metal. $\Delta(RRT)$ therefore represents a change in the retention of the reactant associated only with changes in the active sites.

In certain catalysts, the role played by the geometry of pores and chemistry of surface is critical. For example, in the preparation of multi-functional reforming and platforming catalysts, the control of the volume, surface and size distribution of the pores and of the nature of acidity of the alumina support is very important and difficult to achieve. The conventional specifications, which are non-specific and inadequate, can be usefully supplemented by GC methods. The detailed GSC properties of an ideal support are first determined and then the critical ones are selected and applied as standards on other formulations for rapid and reliable selection.

7. GC TECHNIQUES IN MICRO-REACTORS

The analytical applications discussed above imply discontinuous operation, *i.e.*, they are based on the withdrawal of samples from the catalytic process streams and subjecting them to GC in the laboratory. A more efficient and time-saving method is, however, to carry out catalytic reactions in miniature reactors, which are coupled for automatic operation with a gas chromatograph via pressure regulators and switching valves. The first such successful MR–GC combination was developed in 1955 by Kokes, Tobin and Emmett[5]. In this arrangement, both the components have provision for independent control of temperature, pressure, etc. MR–GC has been used extensively by many workers on various types of gas–solid reactions, as is evident from the extensive review articles by Steingaszner and Pines[160] and Beroza and Coad[161]. Steingaszner and Pines[160] classified microreactors into four categories: (*i*) batch MR operations; (*ii*) intermittant or periodic MR operations (slug or pulse technique); (*iii*) steady-flow MR operations (tail-gas technique); and (*iv*) special MR techniques for the determination of physico-chemical properties. Each of these MR techniques has its special field of application and limitations. Obviously, the choice of an MR–GC apparatus for a given application must follow a thorough understanding of the distinctive features of the above technique variations. Steingaszner and Pines[160] also summarized the description, operation and uses of various types of apparatus in each category that has been developed up to 1967. Hall and Emmett[6] modified the microreactor in 1957 for the more rapid and convenient testing of catalysts as well as for detailed kinetic studies. The two modes of operations of the MR–GC technique, namely "pulse or slug" and "tail-gas", can be studied in a single piece of equipment developed by Ettre and Brenner[162]. This apparatus can also be adapted for studying catalytic reactions involving liquid or solid reactants, thermal, photolytic and radiation reactions. The most significant development in the MR–GC technique was that by Harrison, Hall and Rase[163]. Their completely automatic precision microreactor is capable of generating rapid and accurate information on various aspects of catalyst

TABLE 4

EXAMPLES OF REACTIONS STUDIED IN MICRO REACTORS

Title of paper	System studied	Reference
New microcatalytic chromatographic technique for studying catalytic reactions	Cracking of 2,3-dimethylbutane and instrumentation	164
Investigation of reactions along the catalyst bed in flow system of vapour-phase chromatography	Decomposition of methanol into hydrogen and CO and subsequent synthesis	165
An improved microcatalytic technique	Kinetic study of the catalytic hydrogenation of ethylene	6
Studies of hydrogenation of ethylene over copper–nickel alloys	Hydrogenation of ethylene on copper–nickel alloy	166
Reactivities of naphthenes over a platinum reforming catalyst by a GC technique	Reactivities of naphthenes on Pt–alumina–halogen catalyst	10
A chromatographic technique for studying the mechanism of surface catalysis	Decomposition of formic acid on Pd–Celite 545 catalyst	167
Semi-automatic microreactor for catalytic research	Polymerization of propylene and cracking of 2,3-dimethylbutane over silica–alumina cracking catalyst	168
The microcatalytic chromatographic technique and its application to commercial GC	Catalytic transformation of isobutylene on silica–alumina catalyst	162
Catalytic oxidation of methane. Microcatalytic reactor permits rapid screening of catalysts and provides kinetic data	Oxidation of methane studied on various catalysts	169
Thiophene desulphurization by a microreactor technique	Desulphurization reaction	170
Catalytic activities of synthetic molecular sieves	Polymerization of propene on synthetic molecular sieves	171
Catalytic oxidation of hydrocarbons. Tests of single oxides and supported catalysts in a microcatalytic reactor	Oxidation of various C_6–C_6 hydrocarbons, on "metal on Al_2O_3" catalyst	172
Study of the cracking activity of silica–alumina catalysts by the microcatalytic chromatographic technique	Activity testing of silica–alumina catalysts	173
Microcatalytic hydrogenation and dehydrogenation combined with GLC	Dehydrogenation and hydrogenation of various hydrocarbons on Pt–diatomite catalyst	23
Isomerization of butenes on aluminosilicate catalysts. III. Kinetics of isomerization taking place simultaneously with polymerization	Kinetics of isomerization and polymerization of butenes on alumino-silicate catalysts	174
Microcatalytic studies of hydrogenation of ethylene. I. The promoting effect of adsorbed hydrogen on the catalytic activity of metal surfaces	Hydrogenation of ethylene by copper catalyst	175

TABLE 4 (*continued*)

Title of paper	System studied	Reference
Study of different properties of alumino-silicate catalysts by microcatalytic chromatographic technique	Polymerization of ethylene and butylene on aluminosilicate catalyst	176
Reaction GC —determination of skeleton structure by means of reaction GC	Dehydrogenation, hydrogenation and dealkylation of monoterpenes	177
Oxidative dealkylation of alkyl aromatic hydrocarbons —selective vapour-phase catalytic oxidation of alkyl aromatic hydrocarbons to their parent homo-logue	Oxidative dealkylation of aromatic hydrocarbons studied on several catalysts	178
Isomerization and hydrogenation cleavage of paraffins on palladium catalysts	Isomerization and cracking activity of Pd–carrier catalyst	179
Application of GC in studies of the chemisorption of hydrogen on metal surfaces	Hydrogen chemisorption on activated Pt powder	128
An automatic precision microreactor	Design and instrumentation of high pres-sure/temperature microreactor	163
Determination of thiophenic compounds by types in petroleum samples	Non-thiophenic sulphur compounds decomposition over alumina	180
Pulse method for the investigation of the velocity of heterogeneous solid-phase gas reactions combined with GC analysis of reaction products	Kinetics. Heterogeneous gas reactions	42
Catalytic pressure-pulse microreactor	Instrumentation for high-pressure micro-reactor	160
Selectivity of gold for hydrogenation and dehydrogenation of cyclohexene	Hydrogenation of cyclohexene on gold catalyst	182
Studies of hydrogen held by solids. IX. Hydroxyl groups of alumina and silica–alumina as sites for the isomerization of butene	Isomerization of butene by hydroxyl groups of alumina and silica–alumina	183
Studies of the hydrogen held by solids. X. Fluorided aluminas as acid catalysts	Isomerization of cyclopropane and 2,3-dimethylbutane by fluorided alumina catalysts	184
The decomposition of nitrous oxide on chromia–alumina catalysts	Decomposition of nitrous oxide by chromia–alumina catalyst	185
The mechanism of hydrogenolysis and isomerization of hydrocarbons on metals. II. Mechanism of isomerization of hexenes on platinum catalysts	Hydrogenolysis and isomerization of hexenes and methylcyclopentane on platinum catalysts	186
Check on the performance of a commer-cial water–gas shift reaction	Study of re-oxidation of reduced oxide catalyst. Oxidation by oxygen and reduction by carbon dioxide	187
A rapid method for the investigation of solid-phase gas reactions	Investigation of the process of reduction of oxide catalyst by hydrogen	188
Linear free energy relationship in hetero-geneous catalysis. I. Dealkylation of alkylbenzenes on cracking catalysts	Dealkylation of alkylbenzenes on crack-ing catalysts	189
Catalytic hydrogenolysis of ethane over noble metals of Group VIII	Hydrogenolysis of ethane by noble-metal catalysts	190
Integrated system for MR–CG	Instrumentation for high-pressure micro-reactor	191

study. This microreactor can be operated under pressure with fixed or fluidized-bed catalysts.

The major applications of MR–GC that are given in Table 4 include: (*i*) rapid testing, evaluation and scanning of catalyst formulations; (*ii*) rapid establishment of optimized conditions of process and operating variables and rapid acquisition of data for process/plant design; (*iii*) fast comparison of performance and study of activity decline phenomena of catalysts; (*iv*) study of the influence of externally applied fields, such as electrical, magnetic and ionizing radiations, on the performance of catalysts; (*v*) study of the influence of foreign metals and so-called coke deposits on physico-chemical and catalytic properties; (*vi*) investigation of reaction kinetics and mechanisms; and (*vii*) role of the geometry of pores and chemistry of surface in hetero-geneous catalysis. Some of the important advantages derived from the MR–GC technique are the requirement for only a few grams of catalyst and a few microlitres of reactants; immediate analysis of feed and products in the same set-up; efficient following of the qualitative and quantitative changes in the products as catalysts and reaction conditions are varied; instantaneous monitoring of compounds that cause a decline of activity or poisoning of catalysts; a rapid method of comparing the suita-bility and performance of a number of probable catalysts for given reactions; a rapid method for optimizing the process variables of a successful catalyst; rapidly acquiring data for designing a scaled-up reactor for commercial exploitation; and in conclusion, considerable savings in time, efforts, materials and money in the development of industrial catalysis.

The above virtues highlight the urgency for developing a suitable MR–GC facility in every modern R&D catalyst laboratory as a microcatalytic pilot plant. Considering the flexibility of operation and the wide scope for modification to suit any individual application, there is no reason to doubt a good simulation of the operating conditions and a reasonable applicability of the results from an MR–GC to a com-mercial plant.

8. ON-COLUMN CATALYSIS AND CHROMATOGRAPHIC REACTORS

A few limitations of MR–GC techniques were soon discovered, such as im-purities in the feedstock or catalyst poisons generated during reaction unnecessarily complicating kinetic investigations; the necessity for freezing the reactions of rapid processes creates great experimental difficulties; and reactions involving non-volatile compounds cannot be studied. To overcome these and other limitations, a method that simultaneously exploits the catalytic effect and the chromatographic separating power of porous solids was devised and patented by Dinwiddie and Morgan[192]. This concept was developed almost simultaneously by other workers, namely, Bassett and Habgood[14], Magee[193,194], Frederic[195] and Roginskii and coworkers[196–198]. Experimentally, this concept consists of packing the graded solid catalyst in a column, the reactant being injected as a pulse into the continuously flowing carrier gas. The separating power of the catalyst isolates the reactant from the products as soon as they are formed and also the components of the product, and removes them from the reaction zone of the active catalytic sites. As a result, this local deficiency of products in any reaction site will continue until the equilibrium tends towards the generation of more products. This is why substantially higher yields (as much as

25%)[160] over the thermodynamically predicted value under static conditions have been obtained by the on-column catalysis technique. On the strength of this point alone, the chromatographic reactor technique should be given serious and urgent consideration for scaling-up towards commercial exploitation.

Obviously, this revolutionary concept has stimulated great activity in the use of GC in the R&D of catalysts and catalysis during the last six or seven years, one school being devoted to the evolution of mathematical models and the other in devising experimental techniques of chromatographic reactors. Both types of investigations are listed in Table 5. The superimposition of kinetic parameters on the chromatographic bond-broadening processes causes various distortions in the shapes of reactant peaks, depending on whether the reactions are slow or fast, reversible or irreversible. These observations on the recorded gas chromatogram constitute the basis of a mathematical model, from which simplified kinetic expressions have already been derived by a number of workers for both finite and infinite reaction rates. Rigorous mathematics for chromatographic catalytic reactions will, of course, require the use of computers. The extent of conversion of a reactant is governed by such factors as the sharpness of the resultant pulse, the rate of reaction, thermodynamic equilibrium constants, the rate of separation and the resolving power of the catalyst support.

It must be realized that chromatographic catalytic processes are limited to first-order reactions, because the partial pressure of the reactant, which is continuously transformed into products, varies from point to point down the column reactor, and it is only in the first-order reactions that the fractional conversion is independent of pressure. It may, however, be recalled that most organic reactions are first-order or can be made to follow pseudo-first-order kinetics by using a large excess of one of the reactants either in the carrier gas (in hydrogenation–dehydrogenation reactions) or in the fixed phase, when it is non-volatile. Phillips et al.[207] introduced the technique of interrupted flow in "on-column catalysis", in which the flow of carrier gas is stopped for a definite period of time during the passage of thereactant pulse in order to stop the chromatographic band-broadening process, while allowing the catalytic reaction to proceed. Consequently, the products formed appear as sharp peaks superimposed on the band of the reactant. Various classes of reactions and the resulting reaction chromatograms have been treated mathematically by several workers. This technique is claimed to be more suitable for studying two or more parallel first-order reactions, but is of little value with reversible reactions. Very recently, Phillips et al.[209] extended its scope for studying slow processes encountered in hydrocracking, isomerization, polymerization, hydrogen transfer, etc. The concept and potentialities of chromatographic reactors in heterogeneous catalysis were further developed by Langer et al.[208] in 1969. These workers, as well as Berezkin[46], suggested the application of liquid chromatographic column techniques in the study of catalytic and non-catalytic chemical reactions. The present authors suggest the extension of chromatographic catalytic techniques in the following areas:

(a) When different components of a mixed feed stock have distinct optimum reaction temperatures and do not undergo secondary reactions at other temperatures, the technique of "on-column catalysis" can be advantageously operated under programmed-temperature conditions.

(b) When the solid catalyst has inadequate or no separation power for reactants

TABLE 5

EXAMPLES OF ON-COLUMN CATALYSIS IN CHROMATOGRAPHIC REACTORS

Title of paper	System studied	Reference
A GC study of the catalytic isomerization of cyclopropane	A mathematical model for the isomerization of cyclopropane is developed. The reaction studied on Molecular Sieve 13X exchanged with Ni^{2+} catalyst	14
The vapour chromatograph of a labile compound (the system $A \rightleftharpoons B$)	Mathematical model for the first-order rate equation	199
Fixed-bed catalytic conversion apparatus with rotatable feed inlet	Application of apparatus to dehydrogenation of butylenes to butadiene	192
GC study of the rate of Diels–Alder addition	Rate of reaction of aliphatic diene with chloromaleic anhydride as column liquid coated on Johns-Manville C-22 firebrick	200
Chemical reactions under chromatographic conditions	Special features of chemical reaction in a chromatographic reactor	201
Catalytic reactions and catalysts in chromatographic conditions	Cyclohexane–benzene dehydrogenation reaction on Pt catalyst with higher than equilibrium yield	196
Chemical reaction in chromatographic regime	First-order homogeneous reactions and rate equations	197
Kinetics of heterogenous reactions in the pulsed chromatographic range for conditions of ideal, linear chromatography	A theoretical discussion of the kinetics of heterogeneous catalytic reaction	202
The course of a reaction in a chromatographic column	Kinetic expression for the reaction type $A \rightleftharpoons B + C$	194
Kinetics for reactions under chromatographic conditions on heterogeneous surfaces	Kinetic equations for chromatographic reactors are derived by statistical methods	198
Catalytic dehydrogenation under chromatographic conditions	Dehydrogenation of n-butane in chromatographic column containing aluminium chromate	203
The kinetics of catalytic chromatography. I. Retention time and area half-width of the reactant and product under equilibrium conditions	A theoretical equation is derived	204
Chemical reactions in chromatographic column	Dehydrogenation of cyclohexane to benzene in a column packed with a platinum-on-alumina catalyst	205
A theoretical study on GC accompanied by a chemical reaction	Mathematical correlation of the reaction rate with theoretical plates, carrier flow-rate and conversion	206
Performance of chromatographic reactors in cyclic process	Reaction of the type $A \rightleftharpoons B + C$ has been studied and a mathematical model derived for chromatographic reactor	195
A direct study of heterogeneous catalysis by GSC	The reaction cyclopentyl chloride $\longrightarrow$ cyclopentene + HCl	207

TABLE 5 (*continued*)

Title of paper	System studied	Reference
GC methods for studying the kinetics of liquid-phase reactions	1. Reaction between diene and maleic anhydride 2. Reaction of acetic anhydride and alcohol	46
A GC column as a chemical reactor	A theoretical and mathematical treatment	208
Slow process in GC	1. Reaction of *cis*-hept-2-ene and hept-1-ene on a column of $RhClCO(PCl_3)_2$ in diphenylacetonitrile 2. Reaction of but-1-ene with $Al_2(SO_4)_3/Al_2O_3$	209

and products, the same can be incorporated by intimately mixing the catalyst with another suitable non-catalytic GSC or GLC support in the chromatographic reactor. Assuming that one catalytic solid particle has only one active site, by efficient mixing it might be possible, at least in principle, to effect the resolution of reactants and products by the adjacent and new separating particle, before the reactant pulse proceeds to the next active site on another catalyst particle.

(*c*) The chromatographic catalytic technique appears to have a revolutionary potential for industrial catalytic reactions. However, its scale-up to commercial production will have to await satisfactory progress in the technique of industrial scale GC.

9. CONCLUSION

Most researchers on catalysts are aware of the analytical function of GC only. This survey will show them the potentialities of the numerous non-analytical applications of GC in almost all facets of catalysts and catalysis. The serious attention of scientists in the field of GC, catalysis and solid surface is urgently needed for expediting a real breakthrough in bringing the R&D of catalysts from its present status of empiricism to one of rigid science and technology.

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