

Determination of the specific surface area of powders —

**Part 4: Recommendations for methods
of determination of metal surface area
using gas adsorption techniques**

Committees responsible for this British Standard

The preparation of this British Standard was entrusted by the Materials and Chemicals Sector Board to Technical Committee LBI/37, upon which the following bodies were represented:

- BLWA Ltd. (the Association of the Laboratory Supply Industry)
- British Cement Association
- British Coal Corporation
- Coated Abrasives Manufacturers Association
- Guild of Metal Perforators
- Institution of Chemical Engineers
- Institution of Mining and Metallurgy
- Ministry of Defence
- NABIM
- Society of Chemical Industry
- Society of Cosmetic Scientists
- Woven Wire Association

The following bodies were also represented in the drafting of the standard, through a subcommittee:

- Aluminium Federation
- China Clay Association
- Defence Research Agency
- GAMBICA (BEAMA Ltd.)
- Loughborough University of Technology
- Royal Pharmaceutical Society of Great Britain
- Royal Society of Chemistry
- University of Bradford

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Foreword

This Part of BS 4359 has been prepared by Technical Committee LBI/37. Other Parts of the standard are:

- *Part 1: Recommendations for gas absorption (BET) methods;*
- *Part 2: Recommended air permeability methods;*
- *Part 3: (withdrawn) Calculation from the particle size distribution.*

This Part of BS 4359 describes recommended methods for the determination of metal surface area using gas adsorption techniques only and should not be used or quoted as a specification. References to this standard should indicate that the methods used are in accordance with BS 4359-4:1995.

This British Standard calls for the use of substances and/or procedures that may be injurious to health if adequate precautions are not taken. It refers only to technical suitability and does not absolve the user from legal obligations relating to health and safety at any stage.

In particular, attention is drawn to the Health and Safety Executive Control of Substances Hazardous to Health (COSHH) Regulations (1988) [1].

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 16, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

Introduction

Metal catalysts are used extensively in manufacturing processes in for example, the fine chemicals, petrochemical and food industries. These catalysts may be of the supported or Raney type (see 3.8). A non-manufacturing use is that of environmental emission control.

Supported catalysts comprise metal particles located on a support surface. Specific examples include nickel on alumina (hydrogenation), platinum on alumina (reforming) and palladium on carbon (for fine chemicals and hydrogenation). Supported metal catalysts are used in many different physical forms depending on how the reaction is to be conducted, for instance powders, granules, extrudates or monoliths.

Metal catalysts function by providing specific sites for adsorption of reactant molecules on to the surface of metal atoms. Bonds in the reactant become weakened and reaction is facilitated. Desorption of the products from the catalyst leaves the sites available for further reaction.

In straightforward cases, and in the absence of mass transport control, a supported metal catalyst's activity is often proportional to the metal area. However the activity per unit metal area is not always independent of metal particle size.

Laboratory methods for evaluating the metal area of supported metal catalysts include gas adsorption techniques to assess the amount of metal surface that is accessible to the adsorptive molecule. The adsorptive used depends on the nature and application of the catalyst being evaluated.

As with other forms of gas adsorption analysis, static volumetric and flow methods can be used for the evaluation.

1 Scope

This Part of BS 4359 describes recommended methods for the determination of metal surface area using gas adsorption. They are suitable for supported monometallic catalysts where the metal surface area differs from the total surface area. These methods may also be suitable for other metal catalysts, such as some Raney materials. Specific recommendations are given for the determination of metal surface area of nickel, palladium, platinum and copper. Information on the extension of these methods to other metals in Groups VIII and IB of the periodic table is given in Annex A.

Recommendations are made regarding the most suitable gas and test methods for a given metal/support combination.

Both chemisorption methods and those which employ surface reaction (or titration) are described.

Volumetric or flow techniques may be used to determine the amount of gas chemisorbed.

Recommendations are given to correct for any reversible adsorption detected using the volumetric technique.

2 References

2.1 Normative references

This Part of BS 4359 incorporates, by dated or undated reference, provisions from other publications. These normative references are made at the appropriate places in the text and the cited publications are listed on the inside back cover. For dated references, only the edition cited applies; any subsequent amendments to or revisions of the cited publication apply to this Part of BS 4359 only when incorporated in the reference by amendment or revision. For undated references, the latest edition of the cited publication applies, together with any amendments.

2.2 Informative references

This Part of BS 4359 refers to other publications that provide information or guidance. Editions of these publications current at the time of issue of this standard are listed on the inside back cover, but reference should be made to the latest editions.

3 Definitions

For the purposes of this Part of BS 4359, the following definitions apply.

3.1

adsorbate

the adsorbed gas

3.2

adsorption¹⁾

the taking up of one substance, usually gas or liquid, at the surface of another

3.3

adsorption isotherm¹⁾

the relation, at constant temperature, between the amount of substance adsorbed and the equilibrium pressure of the adsorptive

3.4

adsorptive

the gas to be adsorbed

¹⁾ Reproduced from BS 2955.

**3.5
chemisorption²⁾**

adsorption in which the adsorbate is held on the surface by chemical forces

**3.6
metal dispersion**

the ratio of the number of surface metal atoms to the total number of metal atoms

**3.7
metal surface area**

the area of the test sample determined using an adsorptive which adsorbs on the accessible surface of only the metal component of the sample

**3.8
raney metals**

metals (usually nickel, copper or iron) with a porous structure, which are prepared by dissolving out the aluminium from an alloy of the metal and aluminium

**3.9
sintering**

the agglomeration of smaller metal particles to form larger metal particles, causing a reduction in metal surface area

**3.10
stoichiometry**

the number of molecules of adsorbate per surface metal atom

**3.11
surface density**

the number of metal atoms per square metre of the metal surface

**3.12
total surface area**

the area of the test sample determined using an adsorptive which is assumed to adsorb onto all of the accessible surface of the sample

4 Principles**4.1 General**

The basis of the methods is to determine the monolayer amount of adsorbate (e.g. carbon monoxide, oxygen or hydrogen) chemisorbed on the surface of the metal. The experimental design should minimize the extent of multilayer formation, diffusion of adsorbate into the metal, adsorption on the support and damage such as sintering. This is achieved by selecting the adsorptive and experimental conditions (e.g. adsorption temperature, reduction and pretreatment conditions, adsorption or titration) such that the adsorbate is strongly and irreversibly bound to the metal atoms, a form of adsorption known as chemisorption. Adsorption is typically carried out at close to ambient temperature, as under these conditions adsorption on the support and multilayer formation is generally minimized. However, there can still be weakly bound adsorbate associated with chemisorption, which can be compensated for in any of the methods given in this standard. It should be borne in mind that chemisorption may be temperature dependent if the adsorption is activated. This may require an adsorption temperature above ambient. Further information on the mechanism of adsorption onto different adsorbents is available [2], [3]. From the amount of gas adsorbed, the number of chemisorbed molecules can be calculated. Provided the stoichiometry is known, this can be related to the number of accessible metal atoms, from which the metal surface area is calculated.

4.2 Choice of method

The amount of adsorptive which is chemisorbed can be determined using either volumetric or flow methods.

In the volumetric method, chemisorption of the adsorptive on to the sample is carried out in a high vacuum system equipped with calibrated volumes and sensitive pressure measuring devices. The amount of gas chemisorbed at a known temperature and over a range of pressures is measured to determine an adsorption isotherm.

²⁾ Reproduced from BS 2955.

Flow methods are generally carried out at atmospheric pressure using continuous flow or pulsed flow techniques. In the continuous method a gas mixture, comprising an inert carrier and a known concentration of adsorptive, flows over the sample at a known temperature. An adsorptive concentration should be selected which is high enough to saturate completely the sample. Alternatively, the process can be repeated for a range of adsorptive concentrations to generate the adsorption isotherm.

In the pulsed chemisorption method, an inert or reducing gas is allowed to flow over the sample at a known temperature, and a pulse of strongly adsorbing gas is injected into the flow upstream of the sample. If a reducing gas is used, this should not adsorb more strongly than the adsorptive. The exit concentration of the adsorptive is recorded against time. Further pulses of adsorptive are injected into the system until no further adsorption is detected and chemisorption is deemed to be complete.

The volumetric method is generally preferred, especially when it is desired to distinguish between strong and weak chemisorption. However, the flow techniques are more rapid because it is not necessary to determine the free space; they can be applied with equal validity provided care is taken with the interpretation of results. The applicability of flow techniques can be confirmed by the volumetric method. For the determination of copper surface area by dinitrogen oxide (nitrous oxide) decomposition only flow techniques are recommended.

4.3 Choice of adsorptive

Selection of an adsorptive should be based on the need to minimize adsorption on the support, formation of multilayers, and dissolution of gas in the metal. In addition, the stoichiometry should be known. The preferred adsorptive for nickel and platinum is hydrogen, because it can be assumed that there is one atom chemisorbed per metal site. However, for palladium, hydrogen can dissolve in the metal to form a solid solution and, in the case of palladium and platinum, there can be significant quantities of hydrogen located on the support. Alternatively carbon monoxide can be used for platinum and palladium, but the stoichiometry depends on the metal and is a function of metal particle size.

For platinum and palladium, hydrogen-oxygen titration may be used where oxygen chemisorbed on the metal is titrated with hydrogen. In this case, any hydrogen located on the support or dissolved in the metal is excluded from the analysis. A further advantage is that more hydrogen is consumed in the titration than would be chemisorbed, so increasing the sensitivity of the procedure.

The titration can be carried out using either volumetric or flow methods. However, the volumetric method is suitable only if the support adsorbs the water which is produced. Supports such as silica and alumina will adsorb water whereas, for instance, titania does not. Flow methods are suitable for all supports, although a trap to remove water between the sample and the thermal conductivity detector is required if the support does not adsorb water under the conditions of the test.

For copper, dinitrogen oxide (nitrous oxide) is recommended, as both hydrogen and carbon monoxide are too weakly adsorbed and oxygen readily reacts with the subsurface.

Whichever adsorptive is chosen, the purity of all gases should be not less than 99.99 % (V/V). It is recommended that all gases, particularly carrier gases in the flow methods, should be passed through moisture and oxygen traps where appropriate.

5 Sample preparation

5.1 Sampling

The sample to be analysed should be taken representatively from the bulk material. For powders or bulk samples BS 3406-1 should be consulted for suitable apparatus and procedures.

5.2 Sample mass

The mass of sample to be used depends upon the expected metal surface area or total metal loading, and the type of chemisorption equipment used. Typically between 0.1 g and 1.0 g of sample is used for analysis.

5.3 Sample form

The sample can be analysed as a powder or preform (e.g. granule, sphere, extrudate or tablet). If the preform has a homogeneous composition, it can be advantageous to grind the sample to minimize gas transport limitations. If of non-homogeneous composition, whole particles should be used, with a correspondingly larger sample tube.

If a packed bed is used in a flow system, the internal diameter of the sample cell should be at least 5 times the approximate equivalent spherical diameter of the sample particle.