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Nanotechnologies — Nanostructured porous alumina as catalyst support for vehicle exhaust emission control — Specification of characteristics and measurement methods

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Foreword

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This document was prepared by Technical Committee ISO/TC 229, *Nanotechnologies*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Nanostructured porous alumina as catalyst support for vehicle exhaust emission control plays an important role in automotive exhaust treatment[15]. Three-way catalytic converters (TWCs) have been used in vehicle exhaust control systems worldwide, which can convert carbon monoxide (CO), hydrocarbon (HC) and oxynitride (NOx) into carbon dioxide (CO_2), nitrogen (N_2) and oxygen (O_2). Nanostructured porous alumina has the advantages of a high specific surface area (SSA) and excellent thermal stability, which makes TWCs keep high catalytic activity at a temperature of 900 °C to 1 000 °C in gasoline cars. As one of the most important materials in the catalytic converter[16], nanostructured porous alumina with proper performance is in great demand. In the automotive exhaust treatment field, almost 11,000 tons of porous alumina powders are needed per year.

SSA, specific pore volume, impurities and thermal stability are the main characteristics affecting the performance of nanostructured porous alumina as catalyst support[17]. A high SSA can facilitate homogeneous dispersion of noble metal. A suitable specific pore volume ensures efficient noble metal loading and allows reaction gas to pass through and contact with the catalyst. Impurities can deactivate the noble metal catalyst and thus are harmful. An excellent thermal stability guarantees that TWCs maintain at high activity levels after a long distance running and thus have a prolonged service life. The schematic illustration is shown in Annex A.

The world market demand for nanostructured porous alumina is growing year by year. Currently, however, there are no standards for manufacturers in managing quality control and assurance, and for users in selecting suitable materials for TWCs.

This document provides characteristics and measurements of nanostructured porous alumina as catalyst support for vehicle exhaust emission control. It aims to facilitate worldwide transactions between buyers and sellers of nanostructured porous alumina.

Nanotechnologies — Nanostructured porous alumina as catalyst support for vehicle exhaust emission control — Specification of characteristics and measurement methods

1 Scope

This document specifies characteristics to be measured of nanostructured porous alumina in powder form as catalyst support for vehicle exhaust emission control and their relevant measurement methods. It includes critical characteristics that are required to be measured and additional characteristics that are recommended to be measured, based upon agreement between the interested parties. Measurement methods for each characteristic are recommended.

This document is applicable to nanostructured porous alumina for gasoline-powered cars. It does not apply to characteristics specific for health, the environment and safety issues.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/TS 80004-1, *Nanotechnologies — Vocabulary — Part 1: Core terms*

ISO/TS 80004-6, *Nanotechnologies — Vocabulary — Part 6: Nano-object characterization*

3 Terms, definitions and abbreviated terms

3.1 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/TS 80004-1, ISO/TS 80004-6 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1.1
specific surface area
SSA
absolute surface area of the sample divided by sample mass

[SOURCE: ISO 9277:2010, 3.11]

3.1.2
specific pore volume
volume of open pores per unit mass of a material

3.1.3
pore diameter
diameter of a pore in a model in which the pores typically are assumed to be cylindrical in shape and which is calculated from data obtained by a specified procedure

[SOURCE: ISO 15901-1:2016, 3.15]

3.1.4
apparent density
loose bulk density
dry mass per unit volume of a powder obtained by free pouring under specified conditions

[SOURCE: ISO 9161:2019, 3.1]

3.1.5
tap density
dry mass per unit volume of a powder in a container that has been tapped under specified conditions

[SOURCE: ISO 9161:2019, 3.2]

3.1.6
impurity
metallic or non-metallic element present in a material, but not intentionally added to the material

[SOURCE: ISO 3522:2007, 3.10, modified — "in a material, but not intentionally added to the material" has replaced "but not intentionally added to a metal, and the minimum content of which is not controlled".]

3.1.7
loss on ignition
change in mass of a material held at a specified temperature, excluding the loss due to hygroscopic moisture

[SOURCE: ISO 11323:2010, 8.4, modified — "a material held at a specified temperature" has replaced "an ore held at 1 000 °C".]

3.1.8
ceramic honeycomb
fine ceramic body having multiple channels typically arranged in a honeycomb structure

[SOURCE: ISO 20507:2014, 2.1.18, modified — Note 1 to entry has been deleted.]

3.2 Abbreviated terms

BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
ICP-AES	inductively coupled plasma atomic emission spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
SSA	specific surface area
TWC	three-way catalytic converters
XRF	X-ray fluorescence spectrometry

4 Characteristics and their measurement methods

4.1 General

Critical and additional characteristics to be measured of nanostructured porous alumina are listed in Tables 1 and 2, respectively.

Although the International Standards given in Tables 1 and 2 are individually applicable to general or specific materials, all the documents are not yet fully validated whether they are specifically applicable to nanostructured porous alumina. Their application shall be validated and decided by the standards users themselves.

As the nanostructured porous alumina is liable to adsorb moisture, its characteristics can be affected by the storage conditions. The sample for measurements should be stored in a dry environment. If not, the buyers and the sellers should agree upon the storage conditions of the samples for comparability of results.

4.2 Critical characteristics and their measurement methods

The critical characteristics listed in Table 1 shall be measured. The measured values of these characteristics shall be provided to the buyers during purchase. The SSA and the specific pore volume shall be measured before and after thermal treatment.

The measurement methods listed in Table 1 should be used.

Table 1 — Critical characteristics and their measurement methods

Characteristics	Units	Measurement methods	Relevant standard(s)
Specific surface area	m^2/g	Gas adsorption method	ISO 18757:2003
Specific pore volume	m^3/kg	Gas adsorption method	ISO 15901-2:2006
Pore diameter	nm	Gas adsorption method	ISO 15901-2:2006
Impurity content	% mass fraction	ICP-OES/-AES	ISO 17942:2014 ISO 10058-3:2008

4.3 Additional characteristics and their measurement methods

The additional characteristics listed in Table 2 should be measured. The measurement methods listed in Table 2 should be used for the individual characteristics.

Table 2 — Additional characteristics and their measurement methods

Characteristics	Measurement methods	Relevant standard
Apparent density	Funnel method	ISO 3923-1:2018
Tap density	Cylinder tapping method	ISO 3953:2011
Particle size	Laser diffraction method	ISO 13320:2020
Loss on ignition	Incineration and gravimetry	ISO 11536:2015

5 Descriptions of characteristics and measurement methods

5.1 General

The following clauses describe the characteristics and associated measurement methods listed in Tables 1 and 2 in more detail.

5.2 Specific surface area

A large SSA of nanostructured porous alumina ensures an appropriate dispersion of the catalyst in a porous alumina. The SSA is the ratio of the surface area of a nanostructured porous alumina sample to the mass of the sample. The SSA of a nanostructured porous alumina sample shall be measured both before and after thermal treatment. The BET[18][19][20] analysis for the gas adsorption method can be applied to the SSA measurements. The measurement procedures can be found in ISO 18757:2003.

The sample shall be dried at an appropriate temperature (recommended at 200 °C to 300 °C) to remove moisture before measurement. The mass of the dried sample is weighed and loaded in an SSA analyser. The result of the SSA is recorded from the analyser, which is calculated based on BET formula.

The thermal treatment shall be made by keeping a dried sample at a certain temperature in the air atmosphere condition (recommended from 1 000 °C to 1 100 °C, from 4 h to 10 h), and then the sample is cooled down to room temperature. The temperature and time can be agreed upon between the buyers and the sellers.

5.3 Specific pore volume

Specific pore volume is one of the parameters reflecting pore structure of alumina, which is the main distribution site of the catalyst. Therefore, appropriate specific pore volume can ensure good dispersion of the catalyst and catalytic activity.

The specific pore volume of a nanostructured porous alumina sample shall be measured both before and after the thermal treatment. Specific pore volume is calculated by a BJH formula that is developed from Kelvin capillary condensation theory. Measurement procedures can be found in ISO 15901-2:2006.

ISO 15901-2:2006 describes measurement procedures for the evaluation of porosity and pore size distribution of solid materials by gas adsorption. It should be applicable to nanostructured porous alumina powder samples since the standard has been developed for solid materials of which the pore diameter ranges from 2 nm to 100 nm.

The thermal treatment shall be made by keeping a dried sample at a certain temperature in the air atmosphere condition (recommended from 1 000 °C to 1 100 °C, from 4 h to 10 h), and then the sample is cooled down to room temperature. The temperature and time can be agreed upon between the buyers and the sellers.

5.4 Pore diameter

Pore diameter is one of the parameters reflecting pore structure of alumina. An appropriate pore diameter can ensure exhaust smooth emission and facilitate catalytic reaction.

The pore diameter of a nanostructured porous alumina sample without the thermal treatment shall be measured. Pore diameter is calculated by a BJH formula that is developed from Kelvin capillary condensation theory. Measurement procedures can be found in ISO 15901-2:2006.

ISO 15901-2:2006 describes measurement procedures for the evaluation of porosity and pore size distribution of solid materials by gas adsorption. It should be applicable to nanostructured porous alumina powder samples since the standard has been developed for solid materials of which the pore diameter ranges from 2 nm to 100 nm.

5.5 Impurity content

Impurities contained in nanostructured porous alumina have a negative effect on the catalyst application. The impurity contents of a nanostructured porous alumina sample without the thermal treatment shall be measured using an appropriate measurement method. The impurity content is the ratio of the mass of the element except alumina contained in a nanostructured porous alumina sample to the mass of the dried sample.

Identification of relevant impurities using XRF is recommended. Generally, the main impurity elements are Si, Fe, Ti, Ca, Na and K.

The content of impurities is required to be measured by an appropriate measurement method, for example:

— ICP-OES is a method to determine the content of all metallic elements and some non-metallic elements[21].

— ISO 17942:2014 provides methods for the determination of impurity content in boron nitride using ICP-OES.

— ICP-AES can also determine the impurity contents of nanostructured porous alumina[22].

— ISO 10058-3:2008 provides methods for the determination of impurity content in magnesite and doromite using ICP-AES.

ICP-OES and ICP-AES are the same methods and the measurement results are equivalent to each other.

5.6 Apparent density

Apparent density of a nanostructured porous alumina affects the rheological behaviour of catalyst slurry when coated on ceramic honeycomb. The apparent density of a nanostructured porous alumina sample without thermal treatment should be measured using an appropriate measurement method.

The apparent density can be measured by the funnel method. The sample shall be dried at an appropriate temperature (recommended at 200 °C to 300 °C) to remove moisture. Then the dried powder, which is in loose condition, is filled into a cup of known volume. The loose condition is obtained by using, when filling the cup, a funnel placed at a specified distance above the cup. The ratio between the mass determined by weighing and the volume represents the apparent density.

ISO 3923-1:2018 specifies procedures of the funnel method for the determination of the apparent density of metallic powders under standardized conditions[23]. This method may be suitable for nanostructured porous alumina.

5.7 Tap density

Tap density of a nanostructured porous alumina affects the fluidity of catalyst slurry when coated on ceramic honeycomb. The tap density of a nanostructured porous alumina sample without thermal treatment should be measured using an appropriate measurement method.

The sample shall be dried at an appropriate temperature (recommended at 200 °C to 300 °C) to remove moisture. A specified amount of powder in a container is tapped by means of a tapping apparatus until there is no further decrease in the volume[24]. The tap density is the mass of a powder sample divided by its final volume.

Measurement procedures can be found in ISO 3953:2011.

5.8 Particle size

The particle size of a nanostructured porous alumina sample should be measured using an appropriate measurement method.

The particle size is frequently measured by a laser diffraction method for characterizing nanostructured porous alumina[25]. ISO 13320:2020 can be applicable to nanostructured porous alumina samples since the standard specifies laser diffraction measurement procedures applicable to powders.

For measurements of particle size of a nanostructured porous alumina, a laser beam is passed through a suspension test specimen where the porous alumina is dispersed at an adequate concentration in a suitable liquid. The light scattered by the particles, at various angles, is measured by multi-element detectors, and numerical values relating to the scattering pattern are recorded for subsequent analysis. These numerical scattering values are then transformed, using an appropriate optical model and mathematical procedure, to yield the proportion of the total volume of particles to a discrete number of size classes forming a volumetric particle size distribution.

Measurement procedures can be found in ISO 13320:2020.

5.9 Loss on ignition

Loss on ignition is used to measure volatile components and organic components in a nanostructured porous alumina sample.

The loss on ignition is the ratio of the mass difference of a nanostructured porous alumina sample in dried powder form between before and after a heat treatment up to a specified high temperature. Gravimetric method is used for determining the loss on ignition[26].The sample is recommended to be kept at 1 000 °C for at least 1 h. The measurement results are usually expressed as % mass fraction.

Measurement procedures can be found in ISO 11536:2015.

6 Reporting

The reporting should contain, but not be limited to, the following information:

a) all the details generally necessary to identify the product tested (product name, chemical name, lot number);

b) a reference to this document, i.e. ISO/TS 23362:2020;

c) the characteristics measured, the measurement results (including an uncertainty statement), the sample preparation and measurement methods taken in accordance with Table 1, and those taken in accordance with Table 2 when agreed upon between the buyers and the sellers;

d) the date of measurement, the name of the measurement laboratory and a statement on the quality system of the measurement laboratory for individual characteristics;

e) supporting data for the measurements, if any;

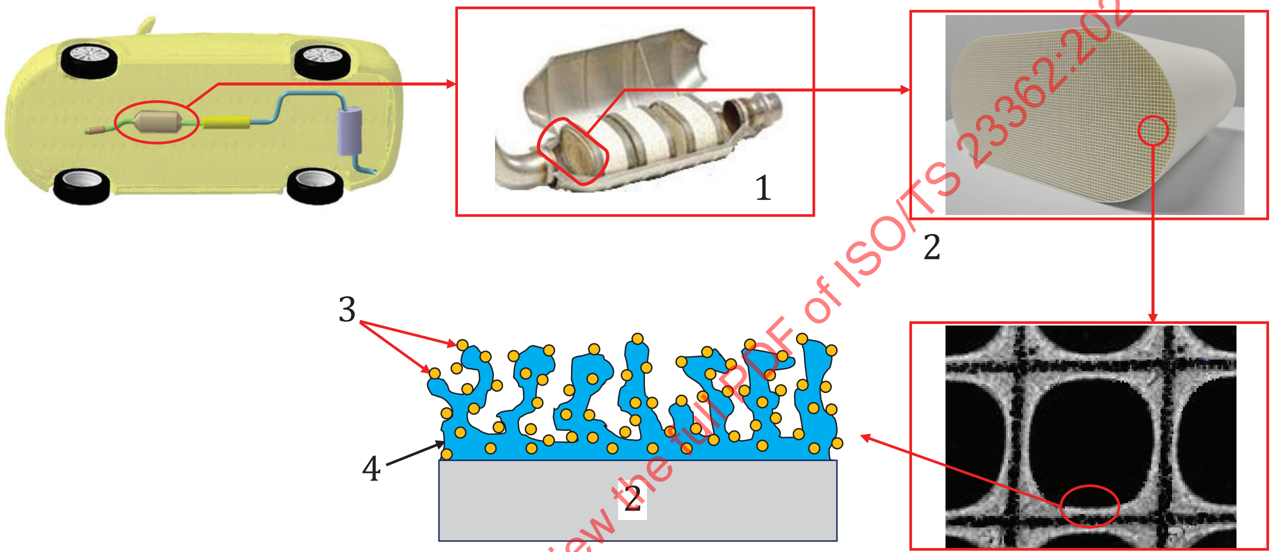
f) deviations from this document, if any, and their justifications.

An example of a reporting table format is shown in Annex B.

Annex A
(informative)

Schematic illustration of three-way catalytic converter

Figure A.1 illustrates the schematic structure of a TWC. It shows that ceramic honeycomb and nanostructured porous alumina play different roles in a TWC.



Key

1 TWC

2 ceramic honeycomb

3 noble metal catalyst

4 nanostructured porous alumina support

Figure A.1 — Schematic illustration of three-way catalytic converter

Annex B
(informative)

Example of reporting table format

Table B.1 shows an example of reporting table format.

The date of measurement, name of the measurement laboratory and statement on the quality system of the measurement laboratory should be provided according to the agreement between the buyer and the seller.

Table B.1 — Reporting table format

<table>
<tr><td colspan="4">General</td></tr>
<tr><td>Product name</td><td></td><td>Chemical name</td><td></td></tr>
<tr><td>Lot number</td><td></td><td>Reference information</td><td></td></tr>
<tr><td colspan="4">Characteristics</td></tr>
<tr><td>Items</td><td colspan="2">Measurement results</td><td>Measurement method</td></tr>
<tr><td>Specific surface area (m^2/g)</td><td colspan="2"></td><td></td></tr>
<tr><td>Specific surface area: after thermal treatment (m^2/g)</td><td colspan="2"></td><td></td></tr>
<tr><td>Specific pore volume (m^3/kg)</td><td colspan="2"></td><td></td></tr>
<tr><td>Specific pore volume: after thermal treatment (m^3/kg)</td><td colspan="2"></td><td></td></tr>
<tr><td>Pore diameter (nm)</td><td colspan="2"></td><td></td></tr>
<tr><td>Apparent density (kg/m^3)</td><td colspan="2"></td><td></td></tr>
<tr><td>Tap density (kg/m^3)</td><td colspan="2"></td><td></td></tr>
<tr><td>Particle size (µm)</td><td colspan="2"></td><td></td></tr>
<tr><td>Loss on ignition (% mass fraction)</td><td colspan="2"></td><td></td></tr>
<tr><td colspan="4">Impurity contents</td></tr>
<tr><td>Items</td><td colspan="2">Analysis data</td><td>Measurement method</td></tr>
<tr><td>Si (% mass fraction)</td><td colspan="2"></td><td></td></tr>
<tr><td>Fe (% mass fraction)</td><td colspan="2"></td><td></td></tr>
<tr><td>Ti (% mass fraction)</td><td colspan="2"></td><td></td></tr>
<tr><td>Ca (% mass fraction)</td><td colspan="2"></td><td></td></tr>
<tr><td>Na (% mass fraction)</td><td colspan="2"></td><td></td></tr>
<tr><td>K (% mass fraction)</td><td colspan="2"></td><td></td></tr>
</table>