

USE OF A MOLYBDENUM-BASED CATALYST FOR THE
DIRECT OXIDATION OF SULPHUR COMPOUNDS TO SULPHUR
AND/OR SULPHATES AT LOW TEMPERATURE

5 The present invention relates to catalysts
for the treatment of gases, especially of industrial
gaseous effluents containing sulphur compounds, with a
view to the catalytic conversion of these compounds to
compounds that can be easily removed.

10 It relates more particularly to catalysts for
the direct oxidation of hydrogen sulphide to sulphur
and/or to sulphates.

Desulphurization of gases containing low
concentrations of hydrogen sulphide has experienced
15 notable development. This treatment is applied in
various fields:

- in the case of constraints related to
the protection of the environment, effluents
originating from Claus units, also called "tail
20 gas" are increasingly subjected to an additional
treatment known as tail gas treatment.

The residual compounds in these tail gases
(sulphur vapour, sulphur dioxide, organic sulphur
compounds such as CS_2 , COS) can be removed by
25 hydrogenation to hydrogen sulphide and then this
hydrogen sulphide is converted to elemental
sulphur and/or sulphates.

It is also possible to envisage, at the exit

of the last Claus reactor, using a deliberate shift of the $\text{H}_2\text{S}/\text{SO}_2$ ratio and then passing the effluent over a catalyst allowing the remaining SO_2 to be converted to sulphur via the Claus reaction
 5 $(2 \text{H}_2\text{S} + \text{SO}_2 \rightarrow 3/x \text{S}_x + 2 \text{H}_2\text{O})$. A final stage of direct oxidation of H_2S to sulphur and/or sulphates then completes the treatment;

- deposits (natural gas, geothermal sources) containing gases naturally exhibiting a low
 10 concentration of hydrogen sulphide are also treated. In some cases a desulphurization based on a Claus process is found to be difficult or even impossible and a process for direct conversion of hydrogen sulphide to sulphur and/or sulphates is preferable.

15 The present invention deals with the processes using the final reaction of conversion of hydrogen sulphide to elemental sulphur and/or to sulphates in the presence of oxygen, and in particular at a temperature lower than the dew temperature of
 20 sulphur, i.e. lower than 170°C . The advantage of working at such a temperature is the ability, on the one hand, to recover the sulphur in liquid or solid form in the porosity of the catalyst and, on the other hand, to shift the thermodynamic equilibrium in the direction
 25 which promotes the reaction of sulphur formation.

However, the shortcoming of a process of this kind is that, simultaneously with the formation of

elemental sulphur, sulphur dioxide is frequently produced in parallel, and is not retained on the catalyst, resulting in a loss in the gas purification yield.

5 Thus the catalysts of the prior art do not make it possible to ensure the best possible conversion of H_2S with the maximum selectivities for sulphur and/or sulphates and a minimum one for SO_2 .

 An aim of the present invention is to provide
10 a catalyst which makes it possible to increase the conversion of H_2S while reducing the conversion to SO_2 to a minimum during the direct oxidation of sulphur compounds at low temperature ($T < 170^\circ C$, preferably $T < 150^\circ C$).

15 In particular, an aim of the present invention is to provide a catalyst which makes it possible to obtain a degree of conversion of H_2S close to 100 % and an SO_2 yield close to 0 % in the course of the reaction defined above.

20 With this aim the invention relates to the use, for the direct oxidation of sulphur compounds to sulphur and/or sulphates at a temperature lower than $170^\circ C$, preferably lower than $150^\circ C$, of a catalyst comprising an active phase including molybdenum and a
25 support based on titanium dioxide, zirconia, silica, silica-alumina or alumina, the said silica, silica-alumina and alumina exhibiting a specific surface of at

least 20 m²/g and a total pore volume of at least 0.3 cm³/g.

Other details and advantages of the invention will appear more clearly on reading the description which follows.

The invention relates first of all to the use, for the direct oxidation of sulphur compounds to sulphur and/or sulphates at a temperature lower than 170°C, preferably lower than 150°C, of a catalyst comprising an active phase including molybdenum and a support based on titanium dioxide, zirconia, silica, silica-alumina or alumina, the said silica, silica-alumina and alumina exhibiting a specific surface of at least 20 m²/g and a total pore volume of at least 0.3 cm³/g.

The catalyst according to the invention has a molybdenum-based active phase which may be in the form of at least one oxide or at least one salt of molybdenum, it being possible for the latter to be chosen, for example, from molybdenum nitrate, sulphate or chloride or an ammonium salt.

The molybdenum element content of the catalyst according to the invention is generally at least 1 % by weight relative to the catalyst, preferably not more than 50 %, still more preferably between 2 and 30 %.

The active phase of the catalyst according to

the invention may additionally include at least one element other than molybdenum, chosen from: iron, titanium, nickel, cobalt, tin, germanium, gallium, ruthenium, antimony, niobium, manganese, vanadium, 5 chromium, phosphorus, zinc, bismuth, the alkali metals group, the alkaline-earth metals group, the rare-earths group and yttrium.

As with molybdenum, these elements may be present in the form of oxides or of salts such as 10 sulphates, nitrates or chlorides.

The content of element(s) other than molybdenum may be at most 40 % by weight relative to the catalyst, preferably at most 30 %, still more preferably at most 20 %.

15 The support of the catalyst according to the invention may be based on alumina, zirconia, silica, silica-alumina or titanium dioxide.

The alumina, silica or silica-alumina of the catalyst according to the invention exhibits a specific 20 surface (SS) of at least 20 m²/g, preferably of at least 40 m²/g, still more preferably of at least 100 m²/g. This specific surface is a surface measured by the BET method.

A surface measured by the BET method is 25 understood to mean the specific surface determined by nitrogen adsorption in accordance with ASTM Standard D 3663-78 established from the Brunauer-Emmett-Teller method described in the periodical "The Journal of the

American Chemical Society", 60, 309 (1938).

The alumina, silica or silica-alumina of the support of the catalyst according to the invention additionally exhibits a total pore volume (TPV) of at least 0.3 cm³/g, preferably of at least 0.4 cm³/g, still more preferably of at least 1 cm³/g. This TPV is measured as follows: the value of the grain density and of the absolute density are determined: the grain (Dg) and absolute (Da) densities are measured by the pycnometry method with mercury and helium respectively, and the TPV is given by the formula:

$$\frac{1}{Dg} - \frac{1}{Da}$$

According to a preferred alternative form the alumina, silica or silica-alumina of the catalyst according to the invention exhibits a volume of pores of diameter greater than 100 Å, known as V_{100Å}, greater than 0.3 cm³/g.

The volume of the pores of diameter greater than 100 Å represents the cumulative volume created by all the pores of size greater than a diameter of 100 Å. This volume is measured by the mercury intrusion technique, in which Kelvin's law is applied.

The catalysts according to the invention are usually in the form of beads; nevertheless any form can be envisaged, especially extrudates, crushed products, monoliths and honeycombs.

These catalyst supports can be obtained by any technique known to a person skilled in the art.

Insofar as alumina is concerned, the alumina powder employed as starting material for the
5 preparation of the support may be obtained by conventional processes such as the precipitation or gel process and the process employing rapid dehydration of an alumina hydroxide such as Bayer hydrate (hydragillite). This latter alumina is that preferred
10 in the invention.

If alumina beads are involved, they can originate from forming by coagulation as drops. This type of beads can, for example, be prepared according to the teaching of patents EP-A-0 015 801 or EP-A-
15 0 097 539. The control of the porosity can be carried out in particular according to the process described in patent EP-A-0 097 539 by coagulation as drops of a suspension or of an aqueous dispersion of alumina or of a solution of a basic aluminium salt which is in the
20 form of an emulsion consisting of an organic phase, of an aqueous phase and of a surface agent or of an emulsifier. The said organic phase may, in particular, be a hydrocarbon; the surface-active agent or emulsifier is, for example, Galoryl EM 10@.

25 The supports in bead form can also be obtained by agglomeration of an alumina powder. The agglomeration in bead form is performed directly on the alumina powder using rotational technology. Rotational

technology is intended to mean any equipment in which the agglomeration is performed by placing the product to be granulated in contact and in rotation about itself. The rotary pelletizer and the rotary drum may
5 be mentioned as equipment of this type. This type of process makes it possible to obtain beads with controlled dimensions and pore distributions, these dimensions and these distributions being generally created during the agglomeration stage. The control of
10 the volumes of the pores of given diameter can also be carried out during this agglomeration stage by an appropriate adjustment of the entry flow rate of the alumina powder and optionally of water, of the speed of rotation of the apparatus or during the introduction of
15 a forming initiator.

If the supports are alumina extrudates, they can be obtained by blending and then extrusion of an alumina-based material, it being possible for the said material to originate from the rapid dehydration of
20 hydrogillite or from the precipitation of boehmite or pseudoboehmite alumina. The control of the porosity of the extrudates may be carried out using the operating conditions of blending of this alumina before extrusion. The alumina may also be mixed with pore-
25 forming agents during the blending. To give an example, the extrudates may be prepared by the preparation process described in patent US-A-3,856,708.

If the alumina supports are crushed material, they may originate from the crushing of any type of alumina-based material such as, for example, beads obtained by any type of process (coagulation as drops, 5 rotary pelletizer or drum), or from extrudates. The control of the porosity of this crushed material is performed via the choice of the alumina-based material which is crushed to obtain it.

Whatever the form of the alumina supports, 10 the porosity can be created by various means, such as the choice of the particle size of the alumina powder or the mixing of several alumina powders of different particle sizes. Another method consists in mixing the alumina powder, before or during the agglomeration or 15 extrusion stages, with a compound, called a pore-former, which disappears completely on heating and which thus creates a porosity in the supports.

Pore-forming compounds employed which may be mentioned by way of example are wood flour, charcoal, 20 sulphur, tars, plastics or plastic emulsions such as polyvinyl chloride, polyvinyl alcohols, naphthalene or the like. The quantity of pore-forming compounds which are added is not critical and is determined by the desired pore volume.

25 The support may also include additives to aid processing and additives for improving the final mechanical properties.

Additives conventionally employed in forming techniques may be used in the preparation of the catalyst of the invention. These additives endow the paste obtained by blending with rheological properties which are suited to the forming. By way of example there may be mentioned especially cellulose, carboxymethyl cellulose, carboxyethyl cellulose, tall oil, xanthan gums, surface-active agents, flocculating agents like polyacrylamides, carbon black, starches, stearic acid, polyacrylic alcohol, polyvinyl alcohol, biopolymers, glucose and polyethylene glycol. The quantity of these additives may vary between 0 and 15 % by weight relative to the weight of the catalyst.

It is possible furthermore to use additional constituents capable of improving the mechanical properties of the formulations. These constituents may be chosen from clays, silicates, alkaline-earth metal sulphates, ceramic fibres and asbestos. These constituents may be employed in quantities by weight relative to the support which can range up to 99.5 % by weight, particularly up to 60 %, preferably up to 30 %.

Following the forming, the alumina supports obtained can be subjected to various operations intended to improve their mechanical strength, such as maturing by being kept in an atmosphere of controlled moisture content, followed by calcining and then by impregnation of the support with a solution of one or more acids and a hydrothermal treatment in confined

atmosphere.

Finally, after these various treatments the supports are dried and calcined.

When the catalyst support is based on
5 titanium dioxide it may be obtained by any method of preparation known to a person skilled in the art, for example according to the teaching of documents EP-A-038741 and EP-A-060741.

The catalyst according to the invention may
10 be in the form of beads of diameter between 1 and 10 mm, preferably between 1 and 6 mm, or in the form of extrudates of cross-section of between 0.7 and 5 mm, preferably between 1 and 3 mm.

The deposition of the catalytic phase or in
15 the support may be carried out by any method known to a person skilled in the art. It may be carried out, for example, by impregnating the support already prepared with the catalytically active elements or precursors of these elements, or by mixing catalytically active
20 elements or precursors with alumina or titanium dioxide during the forming of these materials. In the case of alumina the deposition of the catalytic phase in the support can also be carried out by coprecipitation of alumina and of the catalytically active elements or
25 their precursors.

In the case of deposition by impregnation, this is done in a known manner by placing the support in contact with a solution, a sol or a gel including at

least one catalytically active element in the form of oxide or of salt or of one of their precursors.

The operation is generally carried out by soaking the support in a determined volume of solution of at least one precursor of a catalytically active element. A solution of a precursor of a catalytically active element is intended to mean a solution of a salt or compound of the element or of at least one of the elements constituting the catalytic phase, these salts and compounds being decomposable by heat.

The salt concentration of the solution is chosen as a function of the quantity of active phase to be deposited on the support.

The impregnation surface of the active phase is determined by the solution volume which is adsorbed. The adsorbed volume of the catalytic phase is thus equal to the total pore volume of the support to be impregnated. It is also possible to impregnate the support by soaking it in the solution of precursor of a catalytically active element and to remove the excess solution by drip-draining.

According to a preferred method the active phase is deposited by dry impregnation.

The support may subsequently be subjected to an operation of drying and optionally of calcining. For example, the catalyst may be calcined at a temperature which is between 200 and 1000°C, preferably between 300

and 800°C.

It is also possible to repeat these operations with the same support after it has been dried and calcined and to deposit a number of elements successively on the support and on the determined surfaces, which may vary.

Thus, according to an alternative form, an alumina support may be impregnated with a molybdenum compound and calcined. This support may subsequently be treated with another element such as defined above.

When the deposition of the active phase is carried out during the forming, the catalytically active elements or their precursors are mixed with the alumina or titanium dioxide raw material before it is formed.

The invention also relates to the use of the catalyst described above for the direct oxidation of sulphur compounds to elemental sulphur. This use makes it possible in particular to treat effluents containing quantities of H_2S which are lower than 2 % by volume.

The times of contact of the reaction mixture with the catalyst may range from 0.5 to 20 s, preferably from 1 to 10 s, or even from 2 to 8 s, these values being given for the normal conditions of pressure and temperature; the direct oxidation is preferably conducted with a contact time of at least 3 s.

In a first step the gas to be treated, to which oxygen has been added, is passed over the catalyst according to the invention at a temperature of between 50 and 170°C; the temperature is preferably
5 lower than 150°C.

In a second step the sulphur-laden catalyst is purged with the aid of an oxygen-free gas at a temperature of between 200 and 500°C.

This process applies particularly well to the
10 treatment of gaseous mixtures with a low content of H_2S , because the reaction is highly exothermic and a large rise in temperature would, on the one hand, result in the vaporization of at least a part of the sulphur produced by the reaction and, on the other hand, the
15 oxidation of H_2S would be less selective; larger quantities of SO_2 would be formed.

The following examples illustrate the invention without, however, limiting its scope.

EXAMPLES

Preparation of catalysts according to the invention

5 The characteristics of the supports employed are collated in Table 1.

Table 1

	Type	Specific surface (m ² /g)	Total pore volume (cm ³ /g)	Particle size (mm)	V _{100Å} (cm ³ /g)
1	Alumina beads	192	0.71	2.0-3.2	0.45
2	Alumina beads	114	1.05	2.0-3.2	0.92
3	Alumina extrudates	231	0.60	1.6	0.37
4	TiO ₂ extrudates	124	0.36	3.5	0.27

10 Various catalysts are produced by impregnating these supports with different salts. The impregnation is carried out dry. The drying and calcining conditions depend on the nature of the impregnating salt and are shown below:

15

- sulphate: drying: 15 h at 120°C

- calcining: 3 h at 350°C
- nitrate:
 - drying: 15 h at 85°C
 - calcining: 3 h at 500°C
- acetate:
 - drying: 15 h at 120°C
- 5 calcining: 3 h at 400°C
- ammonium hepta-
 - molybdate:
 - drying: 15 h at 120°C
 - calcining: 3 h at 500°C

10 The salts employed for the various metals are
the following:

- molybdenum: ammonium heptamolybdate: $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$
- iron: sulphate or nitrate
- 15 - cobalt: sulphate
- nickel: sulphate or nitrate
- manganese: acetate
- calcium: sulphate
- phosphorus: phosphoric acid

20

The beads impregnated both with molybdenum and with another element were first of all impregnated with this other element and were then dried at 85°C for 15 h. They were subsequently impregnated with ammonium
25 heptamolybdate and then dried at 120°C for 15 h and calcined at 500°C for 3 hours.

Catalysis test

The procedure of the catalysis test takes place in three stages.

5 The catalyst is first of all subjected to a preaging in order to test it in standard use conditions. This preaging is a preliminary sulphating treatment at 140°C by passing for 20 hours an effluent whose mean composition by volume is:

10 1.5 % of H_2S
 2.4 % of O_2
 30 % of H_2O
 66.1 % of N_2

15 The catalyst is next subjected to a regeneration at 300°C by passing for 6 hours an effluent whose mean composition by volume is:

 30 % of H_2O
 70 % of N_2 ,

20

 then passing for 8 hours another effluent whose mean composition by volume is:

 2.6 % H_2S
 30 % H_2O
25 67.4 % of N_2

Lastly, the direct oxidation reaction is

conducted at 140°C by passing an effluent including:

2500 ppm of H_2S

4000 ppm of O_2

30 % H_2O

5 69.35 % of N_2 .

During this last stage the H_2S conversion α and the SO_2 yield β are measured for a reaction time of 3 hours and a contact time of 4 s or 2 s.

The results are collated in Table 2.

Table 2

	Contact time: 4 s		Contact time: 2 s	
Catalyst composition (nature of the impregnating salt)	α : H ₂ S conversion	β : SO ₂ yield	α : H ₂ S conversion	β : SO ₂ yield
BEADS 1 (alumina)				
3.8 % Ni (sulphate)	98	22	96	26
3.8 % Co	99	34	99	41
3.5 % Mn	35	4	33	4
1.9 % Fe (sulphate)	97	23	86	16
6.9 % Fe (sulphate)	97	81	91	41
5.9 % Mo	100	0	64	0
15.2 % Mo	93	0	66	0
5.9 % Mo 3.3 % Fe (nitrate)	100	25	99	27
10.7 % Mo 1.6 % Fe (nitrate)	100	4	100	13
18.7 % Mo 0.7 % Fe (nitrate)	100	8	100	12
15.0 % Mo 0.5 % Fe (nitrate)	100	12	92	13
14.8 % Mo 1.0 % P	83	4	59	1
BEADS 2 (alumina)				
8.2 % Mo 2.1 % Ni (nitrate)	99	9	100	4
EXTRUDATES 3 (alumina)				
15.1 % Mo 0.29 % Fe (nitrate)	100	8	96	11
15.0 % Mo 0.58 % Fe (nitrate)	100	5	100	15
EXTRUDATES 4 (titanium dioxide)				
3.9 % Fe (nitrate) 4.2 % Ca	100	50	97	43
6.0 % Mo	100	0	67	0

4.1 % Ca				
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It is found that virtually all the molybdenum-based catalysts make it possible to obtain a good total conversion of H_2S while reducing the formation of SO_2 to a minimum.

- 5 On the other hand, the catalysts of the prior art exhibit either a good conversion of H_2S but simultaneously a high yield of SO_2 (like those based on Co, Fe and Ni), or a low yield of SO_2 but a poor conversion of H_2S (like those based on Mn).

CLAIMS

1. Use of a catalyst for the direct oxidation of sulphur compounds to elemental sulphur and/or to sulphates at a temperature lower than 170°C,
5 characterized in that the said catalyst comprises an active phase including molybdenum and a support based on titanium dioxide, zirconia, silica, silica-alumina or alumina, the said silica, silica-alumina and alumina exhibiting a specific surface of at least 20 m²/g and a
10 total pore volume of at least 0.3 cm³/g.
2. Use according to claim 1, characterized in that the direct oxidation is carried out at a temperature lower than 150°C.
3. Use according to claim 1 or 2, characterized
15 in that the active phase of the catalyst includes at least one oxide or salt of molybdenum.
4. Use according to any one of claims 1 to 3, characterized in that the catalyst is in the form of beads of diameter between 1 and 10 mm, preferably
20 between 1 and 6 mm.
5. Use according to any one of claims 1 to 3, characterized in that the catalyst is in the form of extrudates of cross-section of between 0.7 and 5 mm, preferably between 1 and 3 mm.
- 25 6. Use according to any one of claims 1 to 5, characterized in that the molybdenum element content is at least 1 % by weight, preferably at most 50 % by



weight relative to the catalyst.

7. Use according to any one of claims 1 to 6, characterized in that the active phase of the catalyst includes at least one element other than molybdenum,
- 5 chosen from iron, titanium, nickel, cobalt, tin, germanium, gallium, ruthenium, antimony, niobium, manganese, vanadium, chromium, phosphorus, zinc, bismuth, the alkali metals group, the alkaline-earth metals group, the rare-earths group and yttrium.
- 10 8. Use according to claim 7, characterized in that the content of element(s) other than molybdenum is at most 40 % by weight relative to the catalyst.

