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(54) PROCESS FOR CONVERTING SULPHUR DIOXIDE TO SULPHUR TRIOXIDE

(71) We, **PRODUITS CHIMIQUES UGINE KUHLMANN**, a French Body Corporate of 25 boulevard de l'Amiral Bruix, 75116 Paris, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for converting sulphur dioxide into sulphur trioxide or for converting sulphur trioxide into sulphur dioxide.

In the making of sulphuric acid by the contact process the conversion of sulphur dioxide into sulphur trioxide is usually made in several steps in the presence of catalysts containing vanadium, at a temperature from 400°C to 600°C at a pressure less than or equal to 15 bars.

As a result of legislation for the prevention of pollution, the residual content of sulphur dioxide in the gaseous emissions from processes such as the contact process has had to be made smaller and smaller. Consequently, yields from conversions of SO₂ to SO₃ have to be very high, i.e. of the order of 0.997 to 0.998. Such yields are at present obtained at atmospheric pressure with intermediate absorption of the SO₃ which is formed, or more easily at a pressure of 5 to 15 bars, with or without intermediate absorption of the resultant SO₃.

Catalysts containing vanadium are extremely active and so are used in very small amounts only. Hence it follows that when operations are carried out under pressure the temperature gradient in the catalytic mass is very high. For this reason, control of the thermal stability of the catalytic mass is very difficult. Consequently there are serious risks of degradation of the catalyst as soon as a temperature of around 620°C is exceeded.

There is therefore a need for a catalyst which can be used for the conversion of SO₂ to SO₃, which while possessing good activity

at temperatures of the order of 600°C, can withstand sudden fluctuations of temperature up to 850°C without degradation. 50

The reverse reaction, the conversion of SO₃ to SO₂ at 600°C—850°C, which occurs in particular in the recovery of residual acids and the transformation of the available energy from solar or nuclear reactors, is very slow in the absence of a catalyst. 55

There is also a need for a catalyst which can be used at 600°C—850°C to catalyse the conversion of SO₃ to SO₂. 60

According to the present invention there is provided a process for converting sulphur dioxide into sulphur trioxide or for converting sulphur trioxide into sulphur dioxide, which process is performed in the presence of a catalyst comprising iron, copper, and at least one alkali metal chosen from sodium and potassium, on a siliceous support consisting of silica of tridymite structure. 65

The said catalyst has been found to be useful for the conversion of SO₂ into SO₃ and for the reverse conversion of SO₃ into SO₂ at higher temperatures. 75

Preferably, the atomic ratio of copper to iron in the catalyst is 0.1—0.55:1, more preferably about 0.35:1 and preferably the atomic ratio of said alkali metal to iron in the catalyst is 1.3—3.2:1, more preferably about 2:1. 80

The catalyst used in the process according to the invention can be prepared in the following manner:

a) compounds of iron, of copper, and sodium and/or potassium compounds are mixed; 85

b) the siliceous support is added;

c) the resultant mass is mixed for about 30 minutes with a sufficient amount of water to produce a homogeneous paste—(an adequate water content is from 25 to 35% by weight, preferably about 30% by weight)—, 90

d) the paste is shaped in some suitable

apparatus, an extruder for example, so as to obtain cylindrical catalyst grains with a diameter of approximately 6 mm and a length of approximately 6 to 8 mm;

5 e) the grains are dried in a suitable apparatus, for example an oven or a tunnel furnace, swept by a current of air at 100—110°C;

10 f) the dried grains are then heated at a temperature of from 550° to 750°C, preferably 600—620°C, for 6 to 8 hours, in the presence of a current of air having an SO₂ content of from 4 to 10%.

15 After the heat treatment the amount of iron oxide present, expressed as Fe₂O₃, is from 7 to 15% and more usually from 10 to 12%.

20 The extrusion mentioned under step d) above is given as one example of the way of shaping of the catalyst. For example, the catalyst may also be formed into pellets. In the latter case the drying step e) is performed before the shaping step d).

25 The iron and copper compounds from which the catalyst is made are chosen from the oxides or hydroxides thereof and their anhydrous or hydrous salts with organic or inorganic volatile anions. Examples of organic anion salts which may be used are acetates, formates and malates; examples of suitable inorganic anion salts are sulphates and salts having an anion which is thermally less stable than the sulphate anion, for example a carbonate or a nitrate.

35 The sodium and/or potassium compounds are preferably carbonates, anhydrous hydroxides or hydroxide solutions, sulphates or silicates.

40 The siliceous support used in the catalyst is a silica of tridymite structure. This silica has properties which contribute to the catalytic and mechanical stability of the catalyst when it is used in a process which may entail sudden fluctuations of temperature up to 800—850°C. It should be noted that siliceous supports which tend to assume a cristobalite structure as the temperature rises are not suitable. The average dimension of the particles of said siliceous base is about 75μ and the apparent density is about 0.8, the specific surface is of the order of 50 m²/g and the porosity of the order of 0.8—0.85 cc/g. The amount of siliceous support is preferably 400 to 750, more preferably about 500, parts by weight, to 100 parts by weight of iron.

55 The catalyst used in the process according to the invention, while having good properties of activity in the reaction of conversion of SO₂ to SO₃ and the reverse reaction in their respective ranges of temperature, is capable of withstanding sudden fluctuations of temperature up to 850°C.

The following Examples illustrate the invention. 65

EXAMPLE 1

128.6 g of ferric sulphate Fe₂(SO₄)₃ and 56.2 g of copper sulphate (CuSO₄ · 5H₂O) were introduced into a mixer. To this was added 163.7 g of 40% sodium hydroxide solution. The reagents were intimately mixed and then 180 g of silica of tridymite structure were added. Mixing was continued for 30 minutes until a homogeneous paste was obtained. The resultant paste was put into an extruder. Cylindrical grains of catalyst were obtained having a diameter of 6 mm and a length between 6 and 8 mm. The catalyst grains were dried at 110°C and then heat-treated by being kept at 650°C for 6 hours, being swept by air containing 10% of SO₂. 70 75 80

The rates of conversion of SO₂ to SO₃ obtained with this catalyst on the passage of a gas containing 10% SO₂ and 11% O₂ by volume at a pressure of 1 bar at a velocity of 9,000 l/h/litre of catalyst N.T.P. are 7% at 560°C, 15% at 620°C and 29% at 680°C. 85

EXAMPLE 2

90 The method of operation was as described in Example 1 using a mixture of 100.0 g of Fe₂(SO₄)₃, 43.7 g CuSO₄ · 5H₂O, 80 g of 30% sodium hydroxide solution and 65.3 g of 40% potassium hydroxide solution to which 140 g of silica of tridymite structure were added. 95

Mixing, placing in the extruder, drying, and heat treatment were carried out by the method of operation of Example 1. The rates of conversion of SO₂ to SO₃ obtained with this catalyst under the same operating conditions as in Example 1 are: 100

5.3% at 560°C, 14.1% at 620°C and 25.4% at 680°C. 105

EXAMPLE 3

110 The method of operation was as in Example 1 using a mixture of 17.55 g of copper oxide CuO and 139 g of iron sulphate (FeSO₄ · 7H₂O) to which were added 80.0 g of a 50% sodium hydroxide solution and then 140 g of silica of tridymite structure.

Mixing, placing in the extruder, drying and heat treatment were carried out as in Example 1. 115

The rates of transformation of SO₂ into SO₃ obtained with this catalyst under the same operating conditions as Example 1 are 5.7% at 560°C, 12.8% at 620°C and 22.5% at 680°C. 120

EXAMPLES 4 and 5

The catalyst of Example 1 was subjected to accelerated ageing by a long heat treatment consisting of maintaining it for 125

100 hours at 650°C with sweeping by air containing 4% SO₂. After treatment the catalyst has the following weight composition:

5	Fe ₂ O ₃	: 11.36%
	CuO	: 3.82%
	Na ₂ O	: 10.00%
	SO ₃	: 39.28%
	SiO ₂	: 35.54%

10 Measurements of the rates of transformation of SO₂ into SO₃ were carried out by the method in Example 1 at a pressure of 1 bar (Example 4) and 6.8 bars (Example 5). The following results were obtained:

	Example	560°C	620°C	680°C
	Example 4:			
	p=1 bar	5.5%	13.5%	26.3%
	Example 5:			
20	p=6.8 bars	22 %	37 %	34 %

EXAMPLE 6

25 A gas containing 50% SO₃ and 50% nitrogen by volume was passed over the catalyst prepared according to Example 1, the rate of passing being 4,000 l/h/litre of catalyst N.T.P.

30 The rates of conversion of SO₃ into SO₂ obtained at atmospheric pressure are as follows: 58% at 800°C, 32% at 735°C and 21% at 680°C.

In the absence of a catalyst the rates of conversion of SO₃ into SO₂ obtained under the same conditions are negligible.

WHAT WE CLAIM IS:—

1. A process for converting sulphur dioxide into sulphur trioxide or for converting sulphur trioxide into sulphur dioxide, which process is performed in the presence of a catalyst comprising iron, copper, and at least one alkali metal chosen from sodium and potassium, on a siliceous support consisting of silica of tridymite structure. 35 40

2. A process according to Claim 1, in which the atomic ratio of copper to iron in the catalyst is 0.1—0.55:1 and the atomic ratio of alkali metal to iron in the catalyst is 1.3—3.2:1. 45

3. A process according to Claim 1 or Claim 2, wherein the siliceous support in the catalyst is present in an amount of from 400 to 750 parts by weight to 100 parts by weight of iron. 50

4. A process according to Claim 1 substantially as described in any one of the foregoing Examples 1 to 6. 55

5. Sulphur trioxide or sulphur dioxide when obtained by a process as claimed in any one of the preceding claims.

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