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(54) CATALYTIC CONVERSION OF AMMONIUM SULPHATE OR BISULPHATE TO SULPHUR DIOXIDE AND AMMONIA

(71) We, INSTITUT FRANCAIS DU PETROLE, a body corporate organised and existing under the laws of France, of 4 avenue de Bois-Preau, 92502 Rueil-Malmaison, 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:—

This invention relates to the catalytic conversion of ammonium sulphate or bisulphate to ammonia and sulphur dioxide.

Thermal decomposition of ammonium sulphate to sulphur dioxide, ammonia and water was described long ago, for example by Smith (Journ. Soc. Chem. Ind.—14—629—1895; 15—3—1896; Comprehensive Treatise on Inorganic and Theoretical Chemistry by J.W. Mellor, Vol. II, pp. 694—709 (new impression 1967), Longmans, Green and Co. editors.

It takes place as from about 360°C when a stream of steam is passed over ammonium sulphate. The probable reactions are:

$$3 \text{NH}_4 \text{HSO}_4 \rightarrow \text{N}_2 + \text{NH}_3 + 3 \text{SO}_2 + 6 \text{H}_2\text{O}$$

$$3(\text{NH}_4)_2 \text{SO}_4 \rightarrow \text{N}_2 + 4 \text{NH}_3 + 3 \text{SO}_2 + 6 \text{H}_2\text{O}$$

These reactions may be used to convert waste ammonium sulphate to sulphur dioxide and ammonia which may thus be recovered.

That decomposition, which takes place with molten ammonium sulphate, is slow even at about 450°C, but can be activated, as stated in U.S. Patent No 3,825,218, by adding, as catalysts, salts of elements selected from copper, iron, cobalt, chromium, manganese and nickel.

However, under these conditions, the decomposition rate increases only to a small extent.

It has now been found that good decomposition of ammonium sulphate and bisulphate can be achieved, even at relatively low temperatures at which the thermal decomposition is

normally negligible, by the addition of molybdenum compound and/or a tungsten compound, in catalytic amount.

Accordingly, the invention provides a process for converting molten ammonium sulphate or bisulphate to ammonia and sulphur dioxide, which comprises heating ammonium sulphate or bisulphate in contact with a catalyst selected from molybdenum and/or tungsten compounds, at a temperature sufficient for melting of the heated material, and collecting evolved ammonia and sulphur dioxide.

The decomposition may be conducted by adding to a bath of molten ammonium sulphate, from 0.01 to 10% by weight of molybdenum and/or tungsten compounds, for example molybdenum and/or tungsten sulphides and/or oxides, metal molybdates and/or tungstates, for example alkali metal or alkaline-earth metal molybdates and/or tungstates, particularly ammonium molybdate and/or tungstate.

Other specific examples of usable molybdenum compounds are: molybdenum trichloride, tetrachloride, hydroxide, trioxide, pentoxide, oxydichloride, metaphosphate, sesquisulphide and disulphide, molybdic acid and sodium molybdate. Examples of usable tungsten compounds are: tungsten pentachloride, hexachloride, trioxide and disulphide, orthotungstic acid and sodium tungstate.

The results obtained with molybdenum compounds, particularly ammonium molybdate, have regularly been found better than those obtained with tungsten compounds.

A silica carrier, or any other inert catalyst carrier, for example coal, may be impregnated with one of these compounds. The molybdenum and/or tungsten content of the carrier is, for example, 0.5—50% by weight. Additional metals, such as those hereinbefore mentioned,

may be present.

The temperature is usually between the melting point of the selected ammonium sulphate and 500°C, for example between 150° 5 and 500°C, preferably between 350° and 500°C.

When operating with a bath of molten material produced by heating ammonium sulphate, it is advantageous to carry away sulphur dioxide by means of a carrier gas stream. The gas may be an inert gas, for example steam, carbon dioxide and/or nitrogen.

The particular embodiment in which the catalyst has been prepared by impregnating an inert carrier with a compound of molybdenum and/or tungsten is useful when treating gas streams that contain entrained particles of ammonium sulphate and/or bisulphate. Any SO₃ vapors present in the gas stream are also 20 thereby reduced to SO₂.

Particular embodiments of the invention are illustrated by the following non-limitative Examples 3, 4 and 6: Examples 1, 2 and 5 are of comparative processes not according to the 25 invention.

EXAMPLE 1 (Comparative)

A bath of 400 g ammonium bisulphate is 30 heated to 400°C. A stream of 500 Nl/h nitrogen is bubbled therethrough. The SO₂ content of the effluent gas is determined by absorption in a sodium hydroxide solution and titration with an iodine solution. The so-determined SO₂ 35 flow rate is 0.05 mole/h.

The same experiment is carried out at 425°C. In that case, SO₂ is formed at a rate of 0.09 mole/h.

40 EXAMPLE 2 (Comparative)

Example 1 is repeated with a bath of ammonium bisulphate containing 1% by weight of copper as Cu SO₄.

45 At 400°C, SO₂ evolves at a rate of 0.075 mole/h.

At 425°C, the rate is 0.14 mole/h.

EXAMPLE 3

50 Example 1 is repeated with a bath of ammonium bisulphate containing 1% b.w. of molybdenum as ammonium molybdate.

55 At 400°C, SO₂ evolves at a rate of 0.6 mole/h.

At 425°C, the evolution is 3.6 mole/h.

It is thus found that molybdenum increases the decomposition rate of ammonium bisulphate much more than copper.

60 EXAMPLE 4

65 Example 1 is repeated with a bath of ammonium bisulphate containing 1% b.w. of tungsten as ammonium tungstate.

SO₂ evolves at the respective rates of 0.15 mole/h at 400°C and 0.6 mole/h at 425°C.

EXAMPLE 5 (Comparative)

70 0.150 liter/hour of a solution containing 4 moles/liter of ammonium sulphate is sprayed through an atomization nozzle into a stream of 500 Nl/h hot nitrogen supplied to the top of a catalytic reactor containing 250 cc of a contact 75 mass formed of silica cylinders agglomerated by tableting (4 mm diameter, 4 mm height, 400 m₂/g surface). The contact mass is maintained at 420°C by electric heating.

80 After a 2-hour starting period, the gas discharged from the reactor is analysed for determining the SO₂, NH₃ and (NH₄)₂ SO₄ contents. These contents are: 0.045 mole/h SO₂, 0.058 mole/h NH₃ and 0.55 mole/h (NH₄)₂ SO₄. 85

EXAMPLE 6

90 Example 5 is repeated, except that the silica mass is replaced by the same volume of a silica mass of same characteristics, impregnated with ammonium molybdate and calcined for 2 hours at 600°C

The molybdenum content is 10% b.w.

95 The temperature of the reactor is maintained at 420°C. After a 2 hour starting period, the analysis of the gas discharged from the reactor is as follows:

SO ₂	0.59 mole/hour	
NH ₃	0.78 mole/hour	100
(NH ₄) ₂ SO ₄	0.005 mole/hour.	

WHAT WE CLAIM IS:—

1. A process for converting molten ammonium sulphate or bisulphate to ammonia and sulphur dioxide, which comprises heating ammonium sulphate or bisulphate in contact with a catalyst selected from molybdenum and/or tungsten compounds, at a temperature sufficient for melting of the heated material, and collecting evolved ammonia and sulphur dioxide. 105

2. A process according to claim 1, in which the catalyst is a molybdenum and/or tungsten compound selected from the sulphides and oxides of molybdenum and/or tungsten. 115

3. A process according to claim 1, in which the catalyst is an ammonium molybdate or tungstate.

4. A process according to claim 1, in which a stream of inert gas is passed through the molten mass. 120

5. A process according to claim 1, in which the catalyst is supported catalyst comprising a catalyst carrier. 125

6. A process according to claim 5, in which the carrier comprises silica.

7. A process according to claim 5, in which an inert gas stream in which particles of ammonium sulphate and/or bisulphate are entrained 130

is passed through a heated catalyst bed.

8. A process according to claim 1, in which the temperature is in the range 350°–500°C.

5 9. A process according to claim 1, in which the catalyst used is substantially the same as that catalyst described in Example 6.

10 10. A process for catalytically converting ammonium sulphate or bisulphate to ammonia and sulphur dioxide, substantially as hereinbefore described with reference to any of Examples 3, 4 and 6.

11. Ammonia produced by a process according to any preceding claim.

12. Sulphur dioxide produced by a process according to any one of claims 1–10. 15

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