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(54) OXIDATION CATALYSTS AND PROCESS FOR PREPARING SAME

(71) We, GULF RESEARCH & DEVELOPMENT COMPANY, a corporation organized and existing under the laws of the State of Delaware, U.S.A., of P.O. Box 2038, Pittsburgh, Pennsylvania 15230, U.S.A. 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: 5

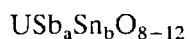
Compounds particularly suitable as oxidation catalysts are prepared using critical amounts of uranium, antimony and tin.

This invention is directed to compounds particularly suitable as oxidation catalysts containing critical amounts of uranium, antimony and tin and to a procedure for preparing the same using critical amounts of said elements. 10

Oxidation catalysts consisting essentially of oxides of antimony and uranium are old and well known. Such catalysts and their uses are described in U.S. Patents Nos. 3,198,750 and 3,308,151 to Callahan and Gertisser. Antimony-uranium oxide catalysts are used primarily for converting propylene, in the presence of ammonia and a gas containing molecular oxygen, to acrylonitrile. Other uses include the ammoxidation of isobutylene to methacrylonitrile and the oxidative conversions of propylene to acrolein, isobutylene to methacrolein, butene-1 or butene-2 to 1,3-butadiene, and isoamylenes to isoprene. It has been shown by Grasselli and Callahan in the *Journal of Catalysis*, 14, 93-103 (1969) that the most effective catalysts are obtained when the antimony to uranium atomic ratio is greater than three. Their best catalyst had an antimony to uranium atomic ratio of 4.6. The sole uranium containing phase detected in this catalyst was USb_3O_{10} according to Grasselli and Suresh, *Journal of Catalysis*, 25, 273-291 (1972). The excess antimony oxide insured that undesirable uranium containing phases such as $USbO_5$ and U_3O_8 were not formed. U.S. Patent No. 3,816,596 to Wise describes a method of making a catalyst consisting essentially of USb_3O_{10} . Antimony-uranium oxide catalysts may be made attrition resistant by adding silica as described in U.S. Patent No. 3,341,471 to Callahan et al. 15 20 25

Attempts have been made to improve the antimony-uranium oxide catalyst by combining the optimum antimony-uranium oxide composition with the oxides of most of the metallic elements of the Periodic Table. See, for example, U.S. Patents Nos. 3,328,315 and 3,431,292 to Callahan et al and British Patent No. 1,007,929 to Distiller's Company Limited. Based on starting materials, every catalyst tested in these patents had an antimony to uranium atomic ratio of 4.0 or 4.6 i.e. close to the optimum composition of Grasselli and Callahan. 30

According to the invention there is provided a catalyst defined by the following stoichiometry: 35



wherein a is from 2.75 to 1.35 and b is from 0.25 to 1.65 wherein the atomic ratios of the sum of antimony and tin to uranium is within a range of 3.5:1 to 2.5:1. 40

Preferably a is from 1.5 to 2.5 and b is from 0.5 to 1.5 and wherein the atomic ratios of the sum of antimony and tin to uranium is within a range of 3.3:1 to 2.7:1.

Further according to the invention there is provided a process for preparing a compound containing uranium, antimony and tin which comprises heating (1) oxides of uranium, antimony and tin, or (2) compounds of said elements that will decompose or be converted 45

to said oxides during said heating, wherein the atomic ratio of antimony to uranium is from 1.35:1 to 2.75:1, the atomic ratio of tin to uranium is from 0.25:1 to 1.65:1 and the atomic ratio of the sum of antimony and tin to uranium is from 2.5:1 to 3.5:1 in an atmosphere containing molecular oxygen at a temperature of at least 800°C for a period of from 15 minutes to 24 hours.

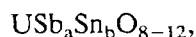
We have found that if we heat for a sufficient length of time at a temperature of at least 800°C an intimate mixture containing (1) oxides of uranium, antimony and tin or (2) compounds of said elements that will decompose or will otherwise be converted to said oxides at said temperature, wherein the atomic ratios of said elements are within selected critical ranges, preferably in molecular oxygen, such as air, we obtain a catalyst in which said elements and oxygen are present within selected critical atomic ratios which catalyst is more highly active as an oxidation catalyst than the prior art catalysts referred to above and which exhibits excellent selectivity in the production of acrylonitrile from propylene.

Examples of oxides that may be heated as part of the mixture described above include UO_2 , U_3O_8 , UO_3 , Sb_2O_3 , Sb_2O_4 , Sb_2O_5 , SnO_2 , SnO , USbO_5 , $\text{USb}_3\text{O}_{10}$. Examples of compounds that will be converted to these oxides upon heating include $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{UO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$, $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$, $\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sb}(\text{C}_2\text{H}_3\text{O}_2)_3$, $\text{Sn}(\text{NO}_3)_4$, SnC_2O_4 , $\text{SnC}_4\text{H}_4\text{O}_6$, and any hydrated oxide or hydroxide of antimony, uranium, or tin.

Intimate mixing of the above materials greatly facilitates the formation of the desired catalyst. In a preferred embodiment of our invention, intimate mixing is achieved by coprecipitation of the hydroxides or hydrated oxides from acidic solution by adding a suitable base such as ammonium hydroxide. The precipitate so obtained is washed with water, dried at a temperature of 100°-200°C. for from two to 24 hours and then calcined. The acidic solution is conveniently prepared using various soluble salts as starting materials. These include $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$, UCl_3 , UCl_4 , UF_6 , UBr_4 , SbCl_3 , $\text{Sb}(\text{C}_2\text{H}_3\text{O}_2)_3$, SbF_3 , SbCl_5 , SnCl_4 and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$.

Alternatively, one can prepare acidic solutions from the metals themselves or their oxides. For example Sb metal can be reacted with concentrated nitric acid to obtain the hydrous oxide, which can be dissolved in concentrated hydrochloric acid.

The amounts of the reactant components used in the preparation of the catalyst herein are critical. Thus the metals in the reactant components must be present in amounts such that the atomic ratio of antimony to uranium is at least 1.35:1, preferably at least 1.5:1, but no higher than 2.75:1, preferably no higher than 2.5:1, the atomic ratio of tin to uranium is at least 0.25:1, preferably at least 0.5:1, but no higher than 1.65:1, preferably no higher than 1.5:1. In addition the atomic ratios of the sum of antimony and tin to uranium must be within a range of 3.5:1 to 2.5:1, preferably 3.3:1 to 2.7:1. We have found that such reactant amounts are critical if we are to obtain the catalysts herein having critical amounts of uranium, antimony, tin and oxygen falling within the following stoichiometric amounts:



wherein a is from 2.75 to 1.35, preferably from 1.5 to 2.5, and b is from 0.25 to 1.65, preferably from 0.5 to 1.5. In addition the atomic ratios of the sum of a and b must be within the range of from 2.5 to 3.5, preferably from 2.7 to 3.3. If amounts outside the reactant amounts are used in the attempted preparation of the new catalysts, the catalysts defined above are not obtained. In such latter case the catalysts so obtained will not have the increased activity and the good selectivity of the catalysts whose stoichiometry is defined above.

Once the critical amounts of reactant components are selected, the reaction mixture containing the same must be heated (calcined) to a critical temperature of at least 800° C., preferably at least 875° C., preferably in an atmosphere containing molecular oxygen in order to obtain the defined catalyst. Although the temperature can be as high as 1050° C., or even higher, in general a temperature of 1000° need not be exceeded. Once having selected a critical temperature within the above range, the mixture is maintained at such temperature for a time sufficient to obtain the catalysts having the defined stoichiometric ratios. At the lower temperatures, longer calcination periods are required, while at the higher temperatures lower periods will suffice. Thus, the time required for calcination can be as low as 15 minutes, generally at least one hour, but a period of no more than 24 hours, generally no more than 18 hours, will suffice. The heating is carried out at atmospheric pressure, although elevated pressures can be used if desired.

The catalyst obtained herein can be employed as an oxidation catalyst using conventional procedures. Thus, in the conversion of propylene to acrylonitrile, in the presence of ammonia and a gas containing molecular oxygen, such as air or oxygen itself, a gaseous mixture containing such reactants is brought into contact with the catalyst defined herein at a pressure of from 0 to 100 pounds per square inch gauge from 0 to 7.0 kilograms per square

centimeter), preferably from 0 to 7.0 kilograms per square centimeter), preferably from 0 to 50 pounds per square inch gauge (from 0 to 3.5 kilograms per square centimeter), in a temperature range of from 375° to 525°C., preferably from 450° to 495°C., at a contact time of at least 0.01 second, preferably in the range of from 0.1 to 15 seconds. The molar ratio of oxygen to propylene is from 0.5:1 to 5:1, preferably from 1:1 to 2:1, while the molar ratio of ammonia to propylene is greater than 0.9:1 but preferably no greater than 1.5:1. By contact time we mean the bulk volume of the catalyst in cubic centimeters divided by the flow rate of the total reactants in vapor form at reaction conditions in cubic centimeters per second. The catalyst herein can be used in a fixed-bed or a fluidized-bed reactor.

10 The following will provide a further understanding of the invention claimed herein. 10

Example I

To a solution containing 91.24 grams of SbCl_3 and 1000 cc. of distilled water there was first added 400 cc. of concentrated HCl and then a solution containing 100.42 grams of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1000 cc. of distilled water. To the resulting solution there was added a solution containing 70.12 grams of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in 1000 cc. of distilled water. The hydrous metal oxides were precipitated from solution by the addition thereto of 1200 cc. of concentrated ammonium hydroxide. The precipitate obtained was filtered, washed with 16 liters of distilled water and then placed in a drying oven for about 16 hours at a temperature of about 120° C. The dried precipitate was then calcined in air at a temperature of 910° C. for 16 hours. In this example, as well as those following, the preparation was carried out at atmospheric pressure and atmospheric temperature. The product obtained had the following stoichiometry: $\text{USb}_2\text{SnO}_{9-10}$. This product falls within the definition of the catalyst herein. Examples II to IV which follow are for comparison purposes

Example II

Example I was repeated except that the following amounts of reactants were used: 35.06 grams of SnCl_4 in 4000 cc. of distilled water, 104.9 grams of SbCl_3 in 1000 cc. of distilled water and 50.21 grams of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 1000 cc. of distilled water. The catalyst obtained possessed the following stoichiometry: $\text{USb}_{4.6}\text{SnO}_x$. This product does not fall within the definition of the catalyst herein.

Example III

Example I was repeated, this time with the following amounts of reactants: 7.36 grams of SnCl_4 in 1000 cc. of distilled water, 104.9 grams of SbCl_3 in 1000 cc. of distilled water and 50.2 grams of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 1000 cc. of distilled water. The product obtained possessed the following stoichiometry: $\text{USb}_{4.6}\text{Sn}_{0.21}\text{O}_x$. This product does not fall within the definition of the novel catalyst herein.

Example IV

To a solution containing 100 cc. of water and 6.84 grams of SbCl_3 there was first added 40 cc. of concentrated HCl and then a solution containing 100 cc. of water and 5.02 grams of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The hydrous metal oxides were precipitated from solution by the addition thereto of 120 cc. of concentrated ammonium hydroxide. The precipitate obtained was filtered, washed with one liter of water and then placed in a drying oven for about 16 hours at a temperature of 120°C. The dried precipitate was then calcined in air at a temperature of 910°C. for 16 hours. In this example, as well as in those following, the preparation was carried out at atmospheric pressure and, unless otherwise stated, at atmospheric temperature. The product obtained, amounting to 7.05 grams, was shown by X-ray diffraction patterns to be the crystalline chemical compound $\text{USb}_3\text{O}_{10}$, with only small amounts (less than about 10 weight per cent, based on the total compounds produced) of Sb_2O_4 and USbO_5 .

Each of the above catalysts (Examples I to IV) was used to prepare acrylonitrile as follows. A 0.5 ml. sample of 20-40 U.S. standard mesh catalyst was weighed and charged to a 0.64 cm. O.D. X 0.48 cm. I.D. tubular stainless-steel microreactor. The reactor was placed in an electric furnace. Air was flowed over the catalyst at the rate of 32.5 cc. STP min^{-1} as the furnace was heated to about 450° C. When the furnace temperature reached 450°C., the reaction was carried out in cyclic fashion. The ammonia and propylene flows were started at 3.0 and 2.5 cc-STP min^{-1} , respectively. The furnace temperature was adjusted so that the reaction temperature located within the catalyst bed was 475°C. After 15 minutes on-stream, the product stream was sampled and then analyzed by gas chromatography. After another 15 minutes on-stream, the propylene and ammonia flows were shut off. The catalyst was regenerated by allowing the air flow to continue for 30 minutes. Propylene and ammonia flows were then resumed to begin the next on-stream period. This procedure was repeated for five or six cycles.

Thus propylene, air and ammonia were reacted at atmospheric pressure in a 1.0:13:1.2 molar ratio at a contact time of 0.28 to 0.29 second.

Average values are reported in Table I for percent conversion, percent selectivity, percent yield, and relative activity. These are defined as:

- 5
- $$\text{Percent Conversion} = \frac{\text{moles of propylene converted}}{\text{moles of propylene fed}} \times 100$$
- 10
- $$\text{Percent Selectivity} = \frac{\text{moles of acrylonitrile produced}}{\text{moles of propylene reacted}} \times 100$$
- $$\text{Percent Yield} = \frac{\text{moles of acrylonitrile produced}}{\text{moles of propylene fed}} \times 100$$
- 15
- $$\text{Relative Activity} = \frac{\text{Ln}(1-X)^{-r}}{(0.3594) (\text{wt. of catalyst})}$$
- 15

where X is the mole fraction of propylene converted.

Table I

Run No.	Catalyst From Example	Stoichiometry			Grams of Catalyst	Mol Per Cent Propylene Converted	Per. Cent Selectivity To Acrylonitrile	Acrylonitrile Yield	Relative Activity
		U	Sb	Sn					
1	I	1.0	2.0	1.0	0.639	95.0	82.0	77.9	13.0
2	II	1.0	4.6	1.0	0.531	19.8	82.5	16.3	1.2
3	III	1.0	4.6	0.21	0.847	38.2	82.8	31.6	1.6
4	IV	1.0	3.0	0	0.495	16.3	80.3	13.1	1.0

The data in Table I amply emphasize the uniqueness of the catalyst of the invention. Note that when a catalyst was employed in Run No. 1 that fell within the definition of the catalyst herein for converting propylene, ammonia and air to acrylonitrile, 95 per cent of the propylene was converted, the yield to desired acrylonitrile was 77.9 per cent and its relative activity was 13.0. When catalysts outside the definition were used in Examples 2 and 3 conversions, acrylonitrile yields and relative activity were low. While the relative activity in Runs Nos. 2 and 3, was only 1.2 and 1.6, respectively. When the base catalyst containing only uranium and antimony was used in Run No. 4, the acrylonitrile yield was only 13.1 per cent and its activity was 1.0.

The catalyst of this invention can be combined with a binder or support, such as silica, in any conventional manner to make the catalyst attrition resistant so that it can be used in a fluidized bed reactor.

Although the novel catalyst herein has been shown to be very effective in the ammoxidation of propylene to acrylonitrile, the catalyst can also be used advantageously in other ammoxidation reactions such as the ammoxidation of isobutylene to methacrylonitrile, and in oxidation reactions, such as oxidation reactions converting propylene to acrolein, isobutylene to methacrolein, butene-1 or butene-2 to 1,3-butadiene, and isoamylenes to isoprene.

WHAT WE CLAIM IS:-

1. A catalyst defined by the following stoichiometry: $USb_aSn_bO_{8-12}$, wherein a is from 2.75 to 1.35 and b is from 0.25 to 1.65 wherein the atomic ratios of the sum of antimony and tin to uranium is within a range of 3.5:1 to 2.5:1

2. The catalyst of claim 1 wherein a is from 1.5 to 2.5 and b is from 0.5 to 1.5 and wherein the atomic ratios of the sum of antimony and tin to uranium is within a range of 3.3:1 to 2.7:1.

3. A process for preparing a compound containing uranium, antimony and tin which comprises heating (1) oxides of uranium, antimony and tin, or (2) compounds of said elements that will decompose or be converted to said oxides during said heating, wherein the atomic ratio of antimony to uranium is from 1.35:1 to 2.75:1, the atomic ratio of tin to uranium is from 0.25:1 to 1.65:1 and the atomic ratio of the sum of antimony and tin to uranium is from 2.5:1 to 3.5:1 in an atmosphere containing molecular oxygen at a temperature of at least 800°C for a period of from 15 minutes to 24 hours.

4. The process of claim 3 wherein the atomic ratio of antimony to uranium is from 1.5:1 to 2.5:1, the atomic ratio of tin to uranium is from 0.5:1 to 1.5:1 and the atomic ratio of the sum of antimony and tin to uranium is from 3.3:1 to 2.7:1.

5. The process of claim 3 wherein the heating temperature is from 875° to 1000°C and the heating time from one to 18 hours.

6. A process wherein propylene is reacted with ammonia and a gas containing molecular oxygen in the presence of a catalyst claimed in claim 1.

7. A process according to claim 6 wherein the catalyst is the catalyst claimed in claim 2.

8. An oxidation catalyst according to Example I.

9. The process for preparing an oxidation catalyst according to Example I.

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