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(54) OXYDEHYDROGENATION CATALYST COMPOSITION

(71) We, UNION CARBIDE CORPORATION, a corporation organized and existing under the laws of the State of New York, United States of America, whose registered office is, 270 Park Avenue, New York, State of New York 10017, United States of America. (Assignees of Frank Glynn Young, Erlind Magnus Thorsteinson). 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 catalyst for use in the gas phase catalytic dehydrogenation of ethane to ethylene in the presence of oxygen, i.e. the oxydehydrogenation of ethane to ethylene.

Ethylene has been conventionally prepared, commercially, by thermally cracking ethane in an endothermic reaction which is carried out at temperatures of about 600° to 1000°C. (U.S. Patent 3,541,179). The reaction time in such process is very short, which makes it difficult or impossible to efficiently recover heat from the process stream. Further, the high temperatures which are used require the use of special alloys in the construction of the furnaces or the reaction vessels in which the reaction is conducted. The cracking reaction also causes the formation of relatively large amounts of low boiling by-products such as hydrogen and methane which complicates, and makes more expensive, the recovery of the ethylene from such by-products.

It is possible to oxydehydrogenate ethane by using a variety of oxyhalogenation catalyst systems in an exothermic reaction. These reactions, however, have only been accomplished at temperatures of at least about 500 to 600°C. (U.S. Patent 3,080,435). Furthermore, the presence of the halogen atoms increases the difficulty of recovering any olefins which are produced. Also, exotic and expensive materials of construction are required to withstand corrosion by the halogens and hydrogen halides in the reaction systems. Further, the halogens themselves must be recovered and recycled to make the system economical.

The oxygehydrogenation of selected $\geqslant C_3$ alkanes, at relatively high temperatures in an exothermic reaction has also been accomplished with selected catalysts which contain vanadium (U.S. Patents 3,218,368, 3,541,179 and 3,856,881) and vanadium and molybdenum (U.S. Patent 3,320,331).

The use of molybdenum and vanadium containing catalyst systems for the gas phase oxidation of alpha-beta unsaturated aliphatic aldehydes, such as acrolein, to the corresponding alpha, beta unsaturated carboxylic acids, such as acrylic acid, has been known. These catalyst systems include those contaning the elements Mo, V and X, where X is Nb, Ti or Ta as disclosed in Belgian Patents 821,322; 821,324 and 821,325.

Prior to the present invention, however, it has not been possible to readily oxydehydrogenate ethane to ethylene at relatively low temperatures with relatively high levels of conversion, selectivity and productivity.

The terms percent conversion, percent selectivity and productivity which are employed herein with respect to the present invention are defined as follows:

$$\%\ \text{conversion (of ethane)} = 100 \times \frac{A}{\text{moles of ethane in the reaction mixture which is fed to the catalyst bed}}$$

Ia wherein A = the molar ethane-equivalent sum (carbon basis) of all carbon-containing products, excluding the ethane in the effluent

II % selectivity (or efficiency for ethylene (or acetic acid) = $100 \times \frac{\text{moles of ethylene (or acetic acid) produced}}{A}$

III productivity for ethylene (or acetic acid) = pounds of ethylene (or acetic acid) produced per cubic foot of catalyst (in the catalyst bed) per hour of reaction time.

According to the present invention there is provided a novel catalyst composition for the vapor phase oxydehydrogenation of ethane to ethylene at relatively low temperatures, the composition comprising the elements Mo, V, Nb and A in the atomic ratio

$$Mo_hV_iNb_jA_k$$

wherein A is one or more of Ce, and U, optionally together with one or more of K, Ni and P.

h is 16

i is 1 to 16, preferably 1 to 8

j is 0.2 to 10, preferably 1 to 10

k is $>$ 0 to 32, preferably 0.1 to 5,

the elements Mo, V, Nb and A being present in combination with oxygen.

The numerical values of h, i, j *and* k represent the relative gram-atom ratios of the elements Mo, V, Nb and A, respectively, which are present in the catalyst composition.

The Catalyst

The elements Mo, V, Nb and A are present in the catalyst composition in combination with oxygen in the form, it is believed of various oxides, as such, and possibly as chemical combinations of oxides such as spinels and perovskites.

The catalyst is preferably prepared from a solution of soluble compounds (salts, complexes or other compounds) of each of the elements Mo, V, Nb and A. The solution is preferably an aqueous system having a pH of 1 to 7, and preferably 2 to 6. The solution of the element-containing compounds is prepared by dissolving sufficient quantities of soluble compounds of each of the elements, so as to provide the desired $h:i:j:k$ gram-atom ratios of the elements Mo, V, Nb and a respectively. To the extent possible the selected compounds of the various elements should be mutually soluble. Where any of the selected compounds of such elements are not mutually soluble with the other compounds, they can be added last to the solution system. The catalyst composition is then prepared by removing the water or other solvent from the mixture of the compounds in the solution system.

The water or other solvent can be removed by evaporation from the mixture resulting from the combination of all the compounds and solvents.

Where the catalyst is to be used on a support, the compounds of the desired elements are deposited on a particulate porous support usually having the following physical properties, but not limited to these: a surface area of 0.1 to 500 square metres per gram; an apparent porosity of 30 to 60%; with at least 90% of the pores having a pore diameter in the range of 20-1500 microns; and the form of the particles or pellets being 1/8 to 5/16 inch in diameter. The deposition is accomplished by immersing the support in the ultimate mixture of all the compounds, evaporating off the major portion of the solvent, and then drying the system at 80 to 220°C. for 2 to 60 hours. The dried catalyst is then calcined by being heated at 220 to 550°C. in air or oxygen for 1/2 to 24 hours to produce the desired

$$Mo_hV_iN_{bj}A_k$$

composition.

The supports which may be used include silica, aluminium oxide, silicon carbide, zirconia, titania and mixtures thereof.

When used on a support, the supported catalyst usually comprises 10 to 50 weight % of the catalyst composition, with the remainder being the support.

The molybdenum is preferably introduced into solution in the form of ammonium salts thereof such as ammonium paramolybdate, and organic acid salts of molybdenum such as acetates, oxalates, mandelates and glycolates. Other water soluble molybdenum compounds which may be used are partially water soluble molybdenum oxides, molybdic acid, and the chlorides of molybdenum.

The vanadium is preferably introduced into solution in the form of ammonium salts thereof such as ammonium metavanadate and ammonium decavanadate, and organic acid salts of vanadium such as acetates, oxalates and tartrates. Other water soluble vanadium compounds which may be used are partially water soluble vanadium oxides, and the sulfates of vanadium.

The niobium is preferably introduced into solution in the form of an oxalate. Other sources of niobium in soluble form, which may be used are compounds in which the metal is co-ordinated, bonded, or complexed to a beta-diketonate, a carboxylic acid, an amine, an alcohol or an alkanolamine.

The uranium and/or cerium (and the potassium and or nickel when used) are preferably introduced into solution in the form of nitrates. Other water soluble compounds of these elements which may be used are the water soluble chlorides and organic acid salts such as acetates, oxalates, tartrates, lactates, salicylates and formates and the carbonates of such elements.

When phosphorus is used it is preferably introduced into the catalyst system as phosphoric acid or as a water soluble phosphate.

It is believed that, for the catalysts to be most effective, the Mo, V, Nb and A metal components should be slightly reduced below their highest possible oxidation states. This may be accomplished during the thermal treatment of the catalyst by the presence of reducing agents such as NH_3 or organic reducing agents, such as the organic complexing agents, which are introduced into the solution systems from which the catalysts are prepared. The catalyst may also be reduced in the reactors in which the oxidation reaction is to be conducted by the passage of hydrogen or hydrocarbon reducing agents such as ethane, ethylene, or propylene through the catalyst bed.

The catalysts, supported or unsupported can be used in a fixed or fluidized bed.

The Ethane

The raw material which is used as the source of the ethane should be a gas stream which contains, at atmospheric pressure, at least 3 volume per cent of ethane. It may also contain minor amounts, i.e., < 5 volume percent, of each of H_2, CO and the C_3-C_4 alkanes and alkenes. It may also contain major amounts, i.e., >5 volume percent of N_2, CH_4, CO_2 and water, as steam.

The catalysts of the present invention appear to be specific with respect to their ability to oxydehydrogenate ethane to ethylene, since the catalysts do not oxydehydrogenate propane, n-butane and butene-1, but rather burn these materials to carbon dioxide, and other oxidized carbonaceous products.

The Reaction Mixture

The components of the gaseous reaction mixture which is used as the feed stream in the process of the present invention and the relative ratios of the components in such mixture are the following:

one mole of ethane,
0.01 to 1/2 mole of molecular oxygen (as pure oxygen or in the form of air), and
0 to 0.4 mole of water (in the form of steam).

The water or steam is used as reaction diluent and as a heat moderator for the reaction. Other materials which may be used as reaction diluents or heat moderators are such inert gases as nitrogen, helium, CO_2, and methane.

During the normal course of the reaction, in the absence of added water, one mol of water is formed per mol of ethane that is oxydehydrogenated. This water that is generated during the reaction will, in turn, cause the formation of some acetic acid, i.e., 0.05 to 0.25 mols, per mol of ethylene that is formed. The water that is added to the feed stream will cause the formation of additional amounts of acetic acid, i.e., up to 0.95 mols of acetic acid per mol of ethylene that is formed.

The components of the reaction mixture are uniformly admixed prior to being introduced into the reaction zone. The components are preheated, individually or after being admixed, prior to their being introduced into the reaction zone, to a temperature of 200 to 500°C.

Reaction Conditions

The preheated reaction mixture is brought into contact with the catalyst composition, in the reaction zone, under the following conditions:

pressure of 1 to 30, and preferably of 1 to 20, atmospheres,
temperature of 150 to 550°C., and preferably, of 200 to 400°C.,

contact time (reaction mixture on catalyst) of 0.1 to 100, and preferably of 1 to 10 seconds, and,

space velocity of 50 to 5000 h^{-1}, preferably 200 to 3000 h^{-1}.

The contact time may also be defined as the ratio between the apparent volume of the catalyst bed and the volume of the gaseous reaction mixture fed to the catalyst bed under the given conditions in a unit of time.

The reaction pressure is initially provided by the feed of gaseous reactants and diluents, and after the reaction is commenced, the pressure may be maintained, preferably, by the use of suitable back-pressure controllers placed on the gaseous effluent side of the catalyst bed.

The reaction temperature is preferably provided by placing the catalyst bed within a tubular converter whose walls are immersed in a suitable heat transfer medium such as tetralin, molten salt mixtures, or other suitable heat transfer agent, which is heated to the desired reaction temperature.

The process of the present invention can be used without added diluents, other than water, to selectively oxydehydrogenate ethane to ethylene and acetic acid to provide % conversion, % efficiencies and productivities, relative to these end products, of the order of

End Product	*(Ethane)* *% Conversion*	*% Efficiency*	*Productivity*
Ethylene (without added H_2O)*	2 to 7	60-85	4 to 7.5
Ethylene (with added H_2O)*	2 to 8	50-80	2 to 8.5
Acetic Acid (without added H_2O)*	2 to 7	15-25	1.5 to 4
Acetic Acid (with added H_2O)*	2 to 8	15-45	2.5 to 5

*i.e. with or without H_2O added to the ethane feed gas

The invention will now be further illustrated by reference to the following Examples which disclose the preparation of various catalyst compositions, and the use of such compositions in the oxydehydrogenation of ethane to ethylene.

The activity of each experimental catalyst was determined in either a microscale U shaped tubular reactor into which a pulsed flow of oxygen and ethane were fed (Test Procedure A); or in a straight tubular reactor in which the ethane and oxygen were concurrently fed continuously (Test Procedure B); These test procedures are described in more detail below.

Catalyst Test Procedure A

Catalysts were screened for activity for the (oxy)dehydrogenation of ethane in a pulse micro-reactor system. The reaction section, a 20″ long by 8 mm diameter silica U-tube, holding the catalyst under test was heated by immersion in a fluidized sand-bath, whose temperature was controlled by a thermocouple controller. The thermocouples for temperature control and measurement were immersed in the fluidized sand, which extended at least three inches above the level of the catalyst in the U-tube. Preliminary exploration of the temperature profile in the sand-bath showed less than a 3-degree variation from top to bottom from the fixed-point set by the controller.

The microreactor was close-coupled to a gas chromatograph for analysis of the product streams. The helium carrier supply flowing through the microreactor was taken from the chromatograph by interrupting the helium-supply line inside the chromatograph at a point directly after the flow-controller, leading it through an 8-port, 2-position valve, [Union Carbide Corporation, Special Instruments Division, Model C4-70], and thence through a 6-port manual sample injection valve [Union Carbide Model 2112-50-2], to the inlet leg of the U-tube reactor. The system was equipped with an injection port holding a rubber septum at the reactor inlet. Product gas from the reactor was led through a cold-trap, back through the 8-port valve, which served to switch the product stream to either of the two analysis systems of the chromatograph. Each valve was equipped with a adjustable by-pass valve to equalize the pressure-drop of the chromatograph column in its analysis system.

Injection of 2.0 ml pulses of feed gas, composition: (% by volume) oxygen 6.5%, ethane 8.0%, balance nitrogen, was made by gas-tight syringe, through the port directly ahead of the catalyst. The gas was diluted and carried over the catalyst, 3.0 grams, by the helium carrier gas, which passed at all times through the reactor at 60 ml/min and through the gas-chromatograph for analysis.

Analysis of the product mixture was made on a 10′ x 1/8″ dia. stainless steel column packed with Poropak (T.M.) R. The column was heated at 10°C/minute, starting at 30°C. Under these conditions the retention times were: air, 2.0 min.; carbon dioxide, 2.5 min.; ethylene, 3.4.; ethane, 4.0 min. The identity of the products was confirmed by chromatography of known pure samples, and by subjecting the separated peaks to mass spectrometric examination. Poropak R is a particulate, spherical shaped polystyrene resin cross-linked with divinylbenzene.

Catalyst Test Procedure B

The catalysts were tested in a tubular reactor under the following conditions: ethane gas feed composition (% by volume), 9.0% C_2H_6, 6.0% 0_2, and 85% N_2; space velocity of 340 hr^{-1}; 1 atm total reaction pressure. As the temperature was raised, the catalyst activity was noted. The reactor consisted of a 1/2″ stainless steel, straight tube heated by means of a molten salt bath (using DuPont HITEC (T.M.) heat transfer salt) of approximately 12″ depth. A 1/8″ thermocouple sleeve ran the entire length of the center of reactor tube and catalyst bed. The catalyst temperature profile could be obtained by sliding the thermocouple through the sleeve. Twenty-six ml of catalyst were introduced into the tube so that the top of the catalyst bed was 4″ below the surface of the heat transfer salt. The catalyst bed was 5-5 1/2″ in length so that it had a depth cross-section ratio >10. The zone above the catalyst bed was filled with glass beads to serve as a preheater. The gaseous effluent from the reactor was passed through a condenser and trap at 0°. The gas and liquid products thus obtained were analyzed as described below.

The reactor inlet and outlet gases from all of the tests conducted under Test Procedure B were analyzed for 0_2, N_2 and CO on a 10′ x 1/8″ column of 5A molecular sieves (14/30-mesh U.S. standard sieve series) at 95°C, and for (0_2, N_2, CO together), CO_2, ethylene, ethane, and H_2O on a 14′ x 1/8″ column of Poropak Q (80/100-mesh) and 95°C. The liquid product (when enough was obtained) was analyzed for H_2O, acetaldehyde, acetic acid, and other components by mass spectroscopy. Poropak Q (T.M.) is a particulate, spherical shaped polystyrene resin cross-linked with divinylbenzene.

In all cases % conversion and % selectivity were based on the stoichiometry:

$$C_2H_6 + 1/2\ O_2 \rightarrow C_2H_4 + H_2O$$

$$C_2H_6 + 7/2\ O_2 \rightarrow 2CO_2 + 3H_2O$$

without applying individual response factors to the eluted peak areas of the chromatograms.

The reaction condition of the two test procedures were as follows:

Catalyst Test Procedure	*Pressure Atmospheres*	*Temp., °C.*	*Contact Time Seconds*	*Space Velocity* hr^{-1}
A	3.3	200 to 650	--	--
B	1	300 - 400	10.6	340

Examples 1 and 2

Catalysts 1 and 2 were prepared as disclosed below, and evaluated in Catalyst Test Procedure B. Each of the catalysts of Examples 1 and 2 contains the elements Mo, V and Nb and one other A element. The composition of each catalyst is given at the heading of the respective Examples, and the test results are given in the Table below.

Each catalyst of Examples 1 and 2 was evaluated at two hot spot temperatures between 300 and 400°C. to determine the % conversion and % efficiency results at each such temperature for oxydehydrogenating ethane to ethylene.

Example 1

$MO_{16}V_8Nb_2Ce_2$ or $Mo_1V_{0.5}Nb_{0.125}Ce_{0.125}$

15.9 Grams of ammonium meta-vanadate (0.136 gram atoms of V) and 48.1 grams of ammonium paramolybdate (0.272 gram atoms of Mo) were dissolved in 0.5 liters of water while stirring at 85-95°C, in a stainless steel steam jacketed evaporating dish.

To the resulting solution were added 31 grams of niobium oxalate solution (14.6% Nb_2O_5) in 100 ml water (0.034 gram atoms Nb) and 14 grams of cerium nitrate (41.8% CeO_2) (0.034 gram atoms Ce) dissolved in 150 ml water.

The resulting mixture was heated while stirring and 150 grams Norton ("Norton" is a registered Trade Mark) silica-alumina #5218 4 x 8 mesh (U.S. Standard sieve series) (irregular shapes) were added. This was followed by drying by evaporation with stirring. Further drying was carried out at a temperature of 120°C for a period of 16 hours.

The dried material was then transferred to a tray fabricated from 10-mesh stainless steel wire screen and calcined in a muffle furnace for 4 hours at 400°C in an ambient atmosphere of air. The amount of catalyst deposited on the support calculated from the weight increase of the catalyst obtained is 28%.

Example 2

$Mo_{16}V_8Nb_2U_1$ or $Mo_1V_{0.5}Nb_{0.125}U_{0.0625}$

15.9 Grams of ammonium metavanadate (0.136 gram atoms of V) and 48.1 grams of ammonium paramolybdate (0.272 gram atoms of Mo) were dissolved in 0.35 liters of water while stirring at 85-95°C, in a stainless steel steam jacketed evaporating dish.

To the resulting solution were added 31 grams of niobium oxalate solution (14.6% Nb_2O_5) (0.034 gram atoms Nb) and 7.2 grams of uranyl acetate, $[(CH_3COO)_2UO_2{\cdot}2H_2O]$ (0.017 gram atoms U).

The resulting mixture was heated while stirring and 140 grams Norton silica-alumina #5218 4 x 8 mesh (irregular shapes) were added. This was followed by drying by evaporation with stirring. Further drying was carried out at a temperature of 120° for a period of 16 hours.

The dried material was then transferred to a tray fabricated from 10-mesh stainless steel wire screen and calcined in a muffle furnace for 4 hours at 400° in an ambient atmosphere of air. The amount of catalyst deposited on the support calculated from the weight increase of the catalyst obtained is 27%.

Table

Results of Tests on Catalysts 1 - 2 by Catalyst Test Procedure B

Example	*Catalyst Composition*	*Metal Oxides in Catalyst, %*	*Catalyst Hot Spot, °C.*	*Ethane Conversion %*	*Efficiency to Ethylene, %*
1	$Mo_{16}V_8Nb_2Ce_2$	28	300	8.6	84
			400	39.4	56
2	$Mo_{16}V_8Nb_2U_1$	27	300	12	91
			400	53	65

Examples 3 - 7

The catalyst of Examples 3 - 7 are outside the scope of the present invention. These catalysts were prepared as disclosed below, and tested in Catalyst Test Procedure A. When so tested they showed little or no selectivity for the purposes of converting ethane to ethylene. The catalysts of Examples 3 - 5 contained excess amounts of Fe and/or Co, i.e., $\geqslant 8$ gram atoms of Fe and/or Co per 16 gram atoms of Mo, and the catalysts of Examples 6 and 7 did not contain any Mo.

Example 3

$Mo_{16}Co_{14}.Mn_2$ or $Mo_1Co_{0.875}Mn_{0.125}$

One thousand five hundred fifty-six (1556) grams of ammonium paamolybdate (8.82 gram atoms of Mo) were dissolved in 4.16 liters of water while stirring at 60-80°C, in a stainless steel evaporating dish.

To the resulting solution were added 178.4 grams of magnanese sulfate (1.06 gram atoms Mn) and 2328 grams of cobaltous nitrate (8 gram atoms Co) dissolved in 1760 ml water.

The resulting mixture was heated while stirring and 633 grams of titanium hydrate pulp was added. The slurry was neutralized with 677 grams of aqueous ammonium dissolved in 1243 ml of water. This was followed by drying by evaporation with stirring on a steam bath. Further drying was carried out at a temperature of 120°C for a period of 16 hours.

The dried material was then transferred to an evaporating desk and calcined in a muffle furnace for 8 hours at 400°C in an ambient atmospere of air. The catalyst was pelletized and then roasted 12 hours at 550°C. Catalyst test results for this material by Procedure A showed no selectivity to ethylene, but complete combustion starting at 210°C.

Example 4

$Mo_{16}Fe_{1.6}Co_{6.4}W_{3.2}Bi_{1.6}Si_{2.16}K_{0.1}$ or

$Mo_1Fe_{0.1}Cr_{0.4}W_{0.2}Si_{0.135}K_{0.006}$

Six hundred forty-eight (648) grams of ammonium paratungstate (2.483 gram atoms of W) and 2124 grams of ammonium paramolybdate (12.03 gram atoms of Mo) were dissolved in 3 liters of water while stirring at 60-80°C, in a stainless steel evaporating dish.

To the resulting solution were added 1400 grams of cobaltous nitrate hexahydrate (4.81 gram atoms of Co), 486 grams of ferric nitrate nonahydrate (1.203 gram atoms of Fe), and 584 grams of bismuth nitrate pentahydrate (1.204 g atoms of Bi), and 300 ml of a 1.35 percent potassium hydroxide solution (0.072 g atoms of K), dissolved in 1400 ml water.

The resulting mixture was heated while stirring and 320 grams of Ludox (Ludox is a registered Trade Mark), a 30.5% colloidal silica sol were added. This was followed by drying by evaporation with stirring on a steam bath. Further drying was carried out at a temperature of 120°C for a period of 16 hours.

The dried material was then transferred to a tray fabricated from 10-mesh stainless steel wire screen and calcined in a muffle furnace for 5 hours at 400°C in an ambient atmosphere of air. The catalyst was mixed with 10 percent of its weight of napthalene and pelleted into 5/16" x 5/16" cylinders. The pellets were roasted 6 hours at 450°C. Catalyst test results for this material by Procedure A showed no selectivity to ethylene on oxidation of ethane at 366°C.

Example 5

$Mo_{16}Fe_8$ *or* $Mo_1Fe_{0.5}$

Thirty-Five point three (35.3) grams of ammonium paramolybdate (0.2 gram atoms of Mo) were dissolved in 200 milliliters of water while stirring at 60-80°C, in a stainless steel evaporating dish. To the resulting solution were added 35 grams of ferric nitrate hexahydrate (0.1 gram atoms of Fe) dissolved in 200 ml water.

The resulting mixture was heated while stirring and then filtered. This was followed by drying at a temperature of 120°C for a period of 16 hours.

The dried material was then transferred to a silica dish and calcined in a muffle furnace for 4 hours at 400°C in an ambient atmosphere of pure oxygen. The amount of catalyst obtained is 34 grams. Catalyst test results for this material by Procedure A showed a reaction beginning at 276°C., but no selectivity for the production of ethylene.

Example 6

$V_3Sb_{12}Ce_1$

Eight point seven (8.7) grams of vanadium pentoxide (0.096 gram atoms of V) was dissolved in 350 ml conc (16N) acid and 200 ml ethanol while stirring at 55°C, in a glass evaporating dish.

To the resulting solution were added 114.4 grams of antimony pentachloride (0.383 gram atoms Sb) dissolved in 80 ml conc HCl and 13.847 grams of cerium nitrate hexahydrate

(0.032 gram atoms Ce) dissolved in 100 ml ethanol.

The resulting mixture was neutralized with 440 ml conc ammonium hydroxide dissolved in 700 ml of water. The precipitate was filtered and washed on the filter with 1000 ml water. This was followed by drying at a temperature of 120°C for a period of 16 hours.

The dried material was then transferred to a tray fabricated from 10-mesh stainless steel wire screen and calcined in a muffle furnace for 12 hours at 750°C in an ambient atmosphere of air. Catalyst test results for this material by Procedure A showed activity to burn ethane at 262°C., but no selectivity for the formation of ethylene.

Example 7

$Sb_5V_1Nb_1Bi_5$

Twenty-eight (28) grams of ammonium metavanadate (0.2404 gram atoms of V) were dissolved in 700 ml of water while stirring at 60-80°C, in a stainless steel evaporating dish.

To the resulting solution were added 583 grams of bismuth nitrate pentahydrate (1.202 gram atoms Bi) and 180 grams of antimony trioxide (1.202 gram atoms Sb) and 219 grams (172 ml) of niobium oxalate sol (0.2404 g atoms Nb) dissolved in 720 ml of 3N nitric acid.

The resulting mixture was heated while stirring and 770 grams (1000 ml) Norton silica-alumina SA5205 1/4″ spheres were added. This was followed by drying by evaporation with stirring on a steam bath. Further drying was carried out at a temperature of 120°C for a period of 16 hours.

The dried material was then transferred to a tray fabricated from 10-mesh stainless steel wire screen and calcined in a muffle furnace for 5 hours at 400°C in an ambient atmosphere of air. The amount of catalyst deposited on the support calculated from the weight increase of the catalyst obtained is 36.1%.

When tested in Catalyst Test Procedure A, the catalyst of Example 7 showed initial activity at 525°C. However, the % selectivity of ethane to ethylene at this temperature was only 26%.

This Application was divided out of Application No. 40560/76 (1,538,107) which claims a process for the catalytic oxydehydrogenation of ethane to ethylene which comprises oxydehydrogenating ethane exothermically in the gas phase at a temperature of $\leqslant 550$°C by contacting the ethane under such conditions with a calcined catalyst composition comprising the elements Mo, X and Y in the ratio

$$MoX_bY_c$$

wherein X is Cr Mn, Nb, Ta, Ti, V and/or W,
Y is Bi, Ce, Co, Cu, Fe, K, Mg, Ni, P, Pb, Sb. Si, Sn, Tℓ and/or U,
b is 0 to 2 and
c is 0 to 2,
with the proviso that the total value of c for Fe, Co Ni is < 0.5.

WHAT WE CLAIM IS:-

1. A calcined catalyst composition comprising the elements Mo, V, Nb and A in the ratio

$$Mo_hV_iNb_jA_k$$

wherein A is one or both of Ce and U,
h is 16,
i is 1 to 16,
j is 0.2 to 10, and
k is > 0 to 32, the elements Mo, V, Nb and A being present in combination with oxygen.

2. A composition as claimed in claim 1, wherein *i* is 1 to 8.
3. A composition as claimed in claim 1 or 2, wherein *j* is 1 to 10.
4. A composition as claimed in claim 1, 2 or 3 wherein *k* is 0.1 to 5.
5. A composition as claimed in any one of claims 1 to 4, wherein A is one or both of Ce and U together with one or more of K, P and Ni.
6. A composition as claimed in claim 1 and substantially as hereinbefore described with reference to either of Examples 1 and 2.

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