

PROCESS FOR THE MANUFACTURE OF ACROLEIN FROM PROPYLENE
BY REDOX REACTION

The present invention relates to the manufacture
5 of acrolein from propylene by oxidation according to a
redox reaction. The invention also relates to the use of
a solid mixed oxide composition as redox system in the
said reaction.

At the present time acrolein is industrially
10 produced by vapour phase catalytic oxidation of
propylene. All the attempts to improve this process have
hitherto been concerned with the development of
catalysts which give the highest possible conversion of
propylene and the highest possible selectivity for the
15 desired acrolein.

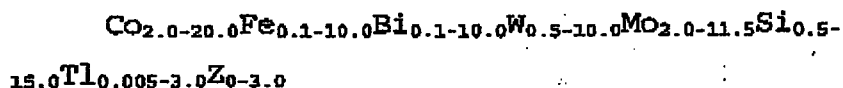
Thus, French Patent No. 2 093 773 describes the
manufacture of acrolein by vapour phase catalytic oxida-
tion of propylene with molecular oxygen in the presence
of an oxide catalyst in which the composition of the
20 catalytic elements, expressed as atomic ratio, is the
following:

$\text{Co}_{2.0-20.0}\text{Fe}_{0.1-10.0}\text{Bi}_{0.1-10.0}\text{W}_{0.5-10.0}\text{Mo}_{2.0-11.5}\text{Si}_{0.5-15.0}\text{Z}_{0.005-1.0}$
with $\text{W} + \text{Mo} = 12.0$ and Z denoting an alkali metal.

This catalyst can be prepared by mixing aqueous
25 solutions of ammonium molybdate and of ammonium
paratungstate, adding solutions of cobalt nitrate, of
iron nitrate and of bismuth nitrate to the aqueous
mixture and then adding an aqueous solution of an alkali
metal hydroxide or carbonate and then colloidal silica
30 as a source of silicon, by moulding the substance
obtained and by calcining it at 350-600°C in a stream of
air.

US Patent No. 3 855 308 describes the
preparation of acrolein by vapour phase catalytic
35 oxidation of propylene with molecular oxygen in the
presence of an oxide catalyst in which the composition

of the catalytic elements, expressed as atomic ratio, is the following:



5 with $W + Mo = 12.0$ and Z denoting an alkali metal or alkaline-earth metal.

The raw materials employed for forming the catalyst may be the oxides of the various metals, but also, depending on circumstances, the nitrates, carbonates or hydroxides. In the case of Mo and W, the salts of acids, such as ammonium molybdate and ammonium tungstate, are recommended. Thus, according to this US patent a catalyst is prepared by mixing aqueous solutions of ammonium molybdate and of ammonium paratungstate
15 respectively, by adding solutions of cobalt nitrate, of iron nitrate and of bismuth nitrate respectively, and then an aqueous solution of alkali metal hydroxide or carbonate and then colloidal silica as a source of silicon, by concentrating the system by evaporation, by
20 adding a support if necessary and by following with an evaporation, a mixing of the resulting substance and a calcination at 350-600°C.

Japanese Patent Showa 45-125 359 describes a vapour phase process for the manufacture of acrolein by
25 catalytic oxidation of propylene with air or oxygen in the presence of a catalyst of formula:



in which:

- $a = 0-20$, $b = 0-20$ with $a + b$ between 0.5 and 20,
- 30 $c = 0.5-8$, $d = 0.1-7$, $0 < e \leq 2$, $h = 0-0.3$, $f = 12$,
 $g = 36-90$;
- Me is one out of Sn, Zn, W, Cr, Mn and Ti; and
- H is at least one out of K, Rb and Cs.

To prepare this catalyst, aqueous solutions of Ni, Co,
35 Fe, K (and/or Rb, Cs), Bi and Me compounds may be added to an aqueous solution of a molybdenum compound

(ammonium molybdate, molybdic acid or molybdenum oxide), then a support such as alumina, silicon carbide and silica (silica sol or silica gel) may be added and then the resulting mixture is heated to dryness, is calcined
5 at approximately 500°C and is converted into pastilles.

French patent No. 2 534 904 describes a catalyst for the manufacture of unsaturated aldehydes, especially acrolein and methacrolein, by vapour phase oxidation of propylene, of isobutylene or of tertiary butanol with a
10 gas containing molecular oxygen. This catalyst is represented by the following formula:



in which:

- A represents nickel and/or cobalt;
- 15 - B represents one or more elements chosen from alkali and alkaline-earth metals and thallium;
- C represents one or more elements chosen from phosphorus, arsenic, boron, antimony, tin, cerium, lead and niobium;
- 20 - D represents one or more elements chosen from silicon, aluminium, zirconium and titanium; and
- a, b, c, d, e, f, g, h and x represent the atomic proportions of the individual elements, and if d is taken as equal to 12: $0.1 \leq a \leq 10$; $0.5 \leq b \leq 10$;
25 $0.1 \leq c \leq 10$; $2 \leq e \leq 20$; $0.001 \leq f \leq 10$;
 $0 \leq g \leq 10$; $0 \leq h \leq 30$; and
- x is the amount of oxygen bound to the other elements and depends on their oxidation states,

bismuth being introduced in the form of an oxide
30 obtained beforehand by calcining, between 600 and 900°C, a mixture of a bismuth compound and a tungsten compound.

The Applicant Company has now discovered that acrolein can be manufactured by gas phase oxidation of propylene in the absence of molecular oxygen by reacting
35 propylene with a particular solid mixed oxide

composition which acts as a redox system and supplies the oxygen necessary for the reaction.

The advantages of this new process, using the redox route and no longer the catalytic route, are the following:

- the limitation of the overoxidation of the products formed, which takes place in the presence of molecular oxygen; according to the present invention, since the operation is carried out in the absence of molecular oxygen, the formation of CO_x (carbon monoxide and carbon dioxide), degradation products, is reduced; and this allows the selectivity for acrolein to be increased, as shown hereinafter by the Comparative Example 4;
- the selectivity for acrolein remains good when the degree of reduction of the solid composition increases;
- once it has undergone a reduction and a gradual loss of its activity, the solid composition can be easily regenerated by heating in the presence of oxygen or of an oxygen-containing gas after a certain period of use; after the regeneration the solid recovers its initial activity and can be employed in a new reaction cycle;
- the separation of the stages of reduction of the solid composition and of its regeneration makes it possible:
 - to increase the selectivity for acrolein; and
 - to increase the partial pressure of propylene, such a partial pressure of propylene feed no longer being limited by the existence of an explosive region of the propylene + oxygen mixture.

The subject-matter of the present invention is therefore firstly the use of a solid mixed oxide composition of formula (I):



in which:

- a is between 0.5 and 5, limits included,
- b is between 0.1 and 10, limits included,
- 5 - c is between 0.5 and 10, limits included,
- d is between 0 and 10, limits included,
- e is between 0 and 15, limits included,
- f is between 0 and 1, limits included,
- g is between 0.1 and 2, limits included, and
- 10 - x is the quantity of oxygen bonded to the other elements and depends on their oxidation states,

in the manufacture of acrolein by propylene oxidation, the said solid composition reacting with the propylene according to the redox reaction (1):



The oxides of the various metals forming part of the composition of the mixed oxide of formula (I) can be employed as raw materials in the preparation of this composition, but the raw materials are not restricted to
20 the oxides; other raw materials which may be mentioned are:

- in the case of molybdenum, ammonium molybdate and molybdic acid,
- in the case of bismuth, iron, cobalt and nickel,
25 the nitrates, carbonates and hydroxides, such as bismuth nitrate, ferric nitrate, cobalt nitrate and nickel nitrate,
- in the case of chromium, chromium nitrate, and
- in the case of potassium, potassium hydroxide,
30 carbonate or nitrate,

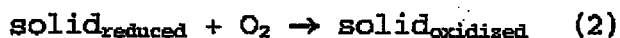
and, in general, any compounds capable of forming an oxide by calcination, namely metal salts of organic acids, metal salts of inorganic acids, metal complex compounds, organometallic compounds and the like.

35 The source of silicon generally consists of colloidal silica.

The subject-matter of the present invention is a process for the manufacture of acrolein from propylene, according to which process gaseous propylene is reacted with a solid composition of formula (I) as defined
5 above, while operating at a temperature of 200 to 600°C, especially from 250 to 450°C, at a pressure of 1.01×10^4 to 1.01×10^6 Pa (0.1 to 10 atmospheres), especially of 5.05×10^4 to 5.05×10^5 Pa (0.5-5 atmospheres), and with a residence time of 0.01 second to 90 seconds,
10 especially of 0.1 second to 30 seconds, in the absence of molecular oxygen, thus carrying out the redox reaction (1) as indicated above.

In accordance with particular embodiments of the present invention the gaseous propylene may be
15 introduced as a mixture with an inert gas such as nitrogen and/or with water (water vapour).

During the redox reaction (1) the solid composition undergoes a reduction and a progressive loss of its activity. This is why, once the solid composition has
20 changed to the reduced state, regeneration of the said solid composition is conducted according to reaction (2):



by heating in the presence of an excess of oxygen or of
25 an oxygen-containing gas at a temperature of 250 to 500°C, for the time necessary for the reoxidation of the solid composition.

After the regeneration, which may be performed in temperature and pressure conditions that are
30 identical with or different from those of the redox reaction, the solid composition recovers an initial activity and can be employed in a new reaction cycle.

The redox reaction (1) and the regeneration can be conducted in a two-stage device, namely a reactor and
35 a regenerator which function simultaneously and in which

two charges of solid composition alternate periodically; the redox reaction (1) and the regeneration can also be conducted in the same reactor by alternating the reaction and regeneration periods.

5 The preparation of acrolein according to the invention is performed according to a stoichiometric and not catalytic reaction.

The following examples illustrate the present invention without, however, limiting its scope. In the formulae shown in these examples x is the quantity of oxygen bonded to the other elements and depends on their oxidation states.

The conversions, selectivities and yields are defined as follows:

15 number of moles of propylene which have reacted

conversion (%) = $\frac{\text{number of moles of propylene which have reacted}}{\text{number of moles of propylene introduced}} \times 100$

$$\text{acrolein (\%)} = \frac{\text{number of moles of acrolein formed}}{\text{number of moles of propylene which have reacted}} \times 100$$

25 selectivity for number of moles of acrylic acid formed
acrylic acid (%) = $\frac{\text{number of moles of acrylic acid formed}}{\text{number of moles of propylene which have reacted}} \times 100$

EXAMPLE 1

30 (a) Preparation of a solid of formula



205.8 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 113.8 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 224.9 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 1.22 g of KNO_3 are dissolved in 420 ml of distilled water at ambient temperature. 76.7 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ are dissolved, also at ambient temperature, in 100 ml of distilled water acidified with 16.67 ml of HNO_3 at a concentration of 68 % by volume.

30.1 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ are dissolved in 20 ml of distilled water, also at ambient temperature. 318.7 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ are dissolved in 900 ml of distilled water at 40°C.

5 The solution containing the bismuth and that containing the chromium are poured successively, with stirring, into the solution containing Co, Ni, Fe and K. The resulting solution is next poured, still with stirring, into the solution containing the molybdenum.

10 23.7 g of colloidal silica (at a concentration of 40 mass%) are then sprinkled into it. The resulting mixture is heated to 80°C for 1.5 hours and is then dried for 12 hours at 140°C. The solid obtained is calcined for 6 hours at 500°C in air. The various metals

15 are present in this solid in the atomic ratios shown in the title of this example.

(b) Preparation of acrolein from propylene by redox reaction

200 mg of this solid are charged into a tubular

20 reactor at 340°C and are then purged with a continuous stream of 11.5 ml/min of helium. 2×10^{-6} mol of propylene are injected onto the solid in order to conduct the redox reaction of the propylene and the solid. The propylene conversion is 93.3 %, with

25 selectivities for acrolein and acrylic acid of 78.0 % and 2.5 % respectively.

EXAMPLE 2

After the reaction of Example 1 (b) has been conducted, the same solid is subjected again to four

30 successive propylene injections in the same test conditions as in Example 1. The performances obtained are reported in Table 1.

Table 1

Injection No.	Propylene conversion (%)	Selectivity for acrolein (%)	Selectivity for acrylic acid (%)
1	88.9	76.8	3.0
2	76.1	76.8	3.3
3	64.5	71.3	3.6
4	56.5	66.7	3.2

EXAMPLE 3

- 5 After the reducing treatment of Example 2 the solid is regenerated for 1 hour in air at 340°C and then replaced under a flow of helium. Four successive new injections of 2×10^{-6} mol of propylene are directed onto the solid in order to conduct the redox reaction of the
- 10 propylene and the solid. The performances obtained are reported in Table 2.

Table 2

Injection No.	Propylene conversion (%)	Selectivity for acrolein (%)	Selectivity for acrylic acid (%)
1	93.0	80.6	3.9
2	84.0	76.7	3.2
3	65.1	70.9	3.5
4	51.6	67.1	2.9

- 15 EXAMPLE 4 (comparative): Preparation of acrolein by the catalytic route

200 mg of a solid prepared according to Example 1 are charged into a tubular reactor at 340°C and are then purged with a continuous flow of 11.5 ml/min of

air. Five injections containing 2×10^{-6} mol of propylene are directed onto the solid, which in this case is the catalyst of the reaction. The propylene conversion is 94.6 % with selectivities for acrolein and acrylic acid of 75.2 % and 3.2 % respectively.

CLAIMS

1. Use of a solid mixed oxide composition of formula (I):



5 in which:



- a is between 0.5 and 5, limits included,
- b is between 0.1 and 10, limits included,
- c is between 0.5 and 10, limits included,
- 10 - d is between 0 and 10, limits included,
- e is between 0 and 15, limits included,
- f is between 0 and 1, limits included,
- g is between 0.1 and 2, limits included, and
- x is the quantity of oxygen bonded to the other
- 15 elements and depends on their oxidation states,

in the manufacture of acrolein by propylene oxidation, the said solid composition reacting with the propylene according to the redox reaction (1):



20 2. Process for the manufacture of acrolein from propylene, characterized in that gaseous propylene is reacted with a solid composition of formula (I) as defined in Claim 1, while operating at a temperature of 200 to 600°C, at a pressure of 1.01×10^4 to

25 1.01×10^6 Pa (0.1 to 10 atmospheres) and with a residence time of 0.01 second to 90 seconds, in the absence of molecular oxygen, thus carrying out the redox reaction (1) as indicated in Claim 1.

3. Process according to Claim 2, characterized in

30 that the gaseous propylene is introduced as a mixture with an inert gas such as nitrogen and/or with water.

4. Process according to either of Claims 2 and 3, characterized in that the redox reaction (1) is conducted at a temperature of 250 to 450°C.

35 5. Process according to one of Claims 2 to 4, characterized in that the redox reaction (1) is conducted at a pressure of 5.05×10^4 - 5.05×10^5 Pa (0.5-5 atmospheres).



6. Process according to one of Claims 2 to 5, characterized in that the redox reaction (1) is conducted with a residence time of 0.1 second to 30 seconds.

5 7. Process according to one of Claims 2 to 6, characterized in that, once the solid composition has changed to the reduced state, the regeneration of the said solid composition is conducted according to reaction (2):

10 $\text{solid}_{\text{reduced}} + \text{O}_2 \rightarrow \text{solid}_{\text{oxidized}} \quad (2)$

by heating in the presence of an excess of oxygen or of an oxygen-containing gas at a temperature of 250 to 500°C, for the time necessary for the reoxidation of the solid composition.

15 8. Process according to Claim 7, characterized in that the redox reaction (1) and the regeneration are conducted in a two-stage device, namely a reactor and a regenerator which function simultaneously and in which two charges of solid composition alternate periodically.

20 9. Process according to Claim 7, characterized in that the redox reaction (1) and the regeneration are conducted in the same reactor by alternating the reaction and regeneration periods.