

Method for producing acrolein

The present invention relates to a process for preparing acrolein from propylene by catalytic gas phase oxidation with molecular oxygen (for example air). The invention further relates to the use of particular propylene-containing starting materials, for example refinery grade propylene, for preparation of acrolein.

Acrolein is used as an intermediate in the industrial scale preparation of the synthetic amino acid DL-methionine and the hydroxy analogue thereof DL-2-hydroxy-4-methylmercaptobutyric acid, which are of considerable economic significance as a feed mix constituent in animal nutrition.

Industrial preparation in the chemical industry is effected very substantially via gas phase oxidation of propane or propylene in the presence of suitable heterogeneous catalysts. This partial oxidation is effected with air as the oxidizing agent at temperatures in the range of about 300 to 400°C, using, for example, tube bundle reactors in which the strongly exothermic reaction is cooled with salt baths. Only a relatively dilute mixture of propylene with air (usually also in the presence of steam) is used, in order to avoid the formation of explosive mixtures. The yields of acrolein achievable with modern catalysts are about 83 to 90% based on propylene (Ullmanns Encyclopedia of Industrial Chemistry, "Acrolein and Methacrolein"); by-products formed are 5 to 10% acrylic acid and 3 to 6% carbon monoxide and carbon dioxide, as well as unconverted propylene.

As well as these, further secondary components are also known, as described, for example in US 6,057,481 and DT 1618889. These include acetaldehyde, formaldehyde, organic acids (e.g. acetic acid), ketones and water.

The occurrence of secondary components depends not only on unselective reactions of the propylene over the catalyst but also strongly on impurities in the propylene used. Propylene is generally obtainable in
5 three qualities which differ by the propylene content, this typically being more than 99.1% for polymer grade, in the range from 92 to 96% for chemical grade and between 50 and 70% for refinery grade (Process Economics Program Report 267, "PROPYLENE PRODUCTION",
10 October 2008). The main secondary component is propane, but also higher saturated and unsaturated hydrocarbons, and also sulphur compounds, as described in Table 4.9 of the aforementioned report.

15 It is likewise stated that refinery grade propylene can be used directly for certain chemical operations, for example in the preparation of cumene or isopropanol. It is mentioned, however, that the concentration of sulphur should not be greater than about 2 ppm (cf.
20 Table 3.2 in Process Economics Program Report 267, "PROPYLENE PRODUCTION", October 2008). This agrees with the patent application US 2004/0192986 A1 to Wu et al., which states that the removal of sulphur components from olefinic hydrocarbon streams leads to an increase
25 in the service life and efficiency of the catalysts in cumene synthesis.

EP 09 595 062 B1 states that saturated hydrocarbons such as propane have only a low reactivity with the
30 catalyst in the conversion of propylene to acrolein (and subsequently to acrylic acid) and thus exert only a low level of influence on the catalyst performance and catalyst service life. What is critical, however, is the presence of unsaturated hydrocarbons in the
35 propylene feed, since they can react with the catalyst under the prevailing conditions and thus lead to by-products, and can worsen the catalyst performance.

It has now been found that, surprisingly, in the preparation of acrolein by catalytic gas phase oxidation of propylene with molecular oxygen, it is possible to employ propylene gas of lower quality without significantly worsening the performance characteristics of the oxidation catalyst used compared to the use of high-quality propylene. It was expected that the yield of acrolein would decline over a prolonged period of operation in the case of use of sulphur components, since side reactions can be enabled by the sulphur compound in the reaction system, or the catalyst is poisoned and selectivity for acrolein thus decreases. More particularly, it has been found that the propylene used, or a propylene-containing reaction gas, may contain sulphur and/or unsaturated hydrocarbons without any significant deterioration in the conversion of propylene and the yield of acrolein compared to the use of propylene without the impurities mentioned.

In addition, refinery grade propylene (75.48% by weight of propylene, 24.04% by weight of propane, 0.28% by weight of ethane, remainder saturated and unsaturated C₂ to C₅ hydrocarbons (excluding C₃ and ethane), 0.7 mg/kg of sulphur, water content below 20 mg/kg) was used as a feed gas for the partial oxidation in the presence of molecular oxygen over a mixed oxide catalyst as described in DE 10 2006 015710 A1. Analogously to the experiments with sulphur component, no significant influence on catalyst performance was found.

The propane present in refinery grade propylene can also be used advantageously firstly as an inter gas (under the conditions described above), and secondly as a fuel gas in a thermal post-combustion connected downstream of the process, which in turn allows a

saving of methane, which is typically used as the fuel gas.

The present invention provides a process for preparing
5 acrolein by catalytic gas phase oxidation, said process comprising the following steps:

- a) providing a reaction gas comprising propylene and molecular oxygen, and
- b) contacting the reaction gas with an oxidation
10 catalyst to form a gas mixture comprising acrolein, the oxidation catalyst being a mixed oxide catalyst comprising or consisting of one or more base components selected from molybdenum, vanadium and tungsten,
15 characterized in that more than 10 ppm by weight of sulphur in the form of any sulphur components is present in the reaction gas provided, but not more than 5000 ppm by weight of sulphur in the form of any sulphur components and not more than 5000 ppm by weight
20 of unsaturated hydrocarbons selected from the group consisting of C_2H_4 , C_3H_4 , C_4H_8 , C_4H_6 , C_5H_{10} , C_5H_8 and mixtures thereof is present in each case in the reaction gas provided.

25 The content of sulphur (in the form of any sulphur components) in the reaction gas provided is determined in accordance with standard EN 24 260 (combustion according to Wickbold). The content of unsaturated hydrocarbons selected from the group consisting of C_2H_4 ,
30 C_3H_4 , C_4H_8 , C_4H_6 , C_5H_{10} , C_5H_8 and mixtures thereof in the reaction gas provided is determined by standard DIN 51619 (gas chromatography). If alternative variants of the procedures are mentioned in the standards, the above-specified ppm by weight values have to be
35 achieved by at least one of the possible alternative variants.

The process according to the invention also allows more than 50 ppm by weight of unsaturated hydrocarbons selected from the group consisting of C_2H_4 , C_3H_4 , C_4H_8 ,
5 C_4H_6 , C_5H_{10} , C_5H_8 and mixtures thereof to be additionally present in the reaction gas provided.

Unsaturated hydrocarbons selected from the group consisting of C_2H_4 , C_3H_4 , C_4H_8 , C_4H_6 , C_5H_{10} , C_5H_8 and
10 mixtures thereof, mean especially ethene, propadiene, methylacetylene, isobutene, 1-butene, cis-2-butene, trans-2-butene, butadiene, 1-pentene and mixtures thereof.

15 In the process according to the invention, the total content of sulphur in the form of any sulphur components in the reaction gas provided may also be more than 20 ppm by weight. It is preferable, however, when the total content of sulphur is not more than
20 1000 ppm by weight.

More particularly, the process according to the invention allows the total content of sulphur in the form of H_2S and/or SO_2 in the reaction gas provided to
25 be more than 20 ppm by weight or else more than 30 ppm by weight or more than 40 ppm by weight, provided that the total content of sulphur in the form of any sulphur components (including H_2S and/or SO_2) in the starting material is preferably not more than 1000 ppm by
30 weight, more preferably not more than 500 ppm by weight, and especially preferably not more than 250 ppm by weight.

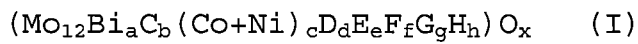
More particularly, the process according to the
35 invention also allows the total content of unsaturated hydrocarbons, selected from the group consisting of C_2H_4 , C_3H_4 , C_4H_8 , C_4H_6 , C_5H_{10} , C_5H_8 and mixtures thereof, in the reaction gas provided to be more than 100 ppm by

weight or else more than 150 ppm by weight or more than 200 ppm by weight, but not more than 1500 ppm by weight, preferably not more than 1300 ppm by weight, and more preferably not more than 1000 ppm by weight.

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In a preferred embodiment of the process according to the invention, the mixed oxide catalyst additionally contains one or more additional components selected from bismuth, antimony, tellurium, tin, iron, cobalt, nickel and copper.

Particularly suitable oxidation catalysts in the context of the present invention are selected from mixed oxide catalysts of the general formula (I) or mixtures of various mixed oxide catalysts of the general formula (I) where:



20 C = iron,

D = at least one of the elements from W, P,

E = at least one of the elements from Li, K, Na, Rb, Cs, Mg, Ca, Ba, Sr,

F = at least one of the elements from Ce, Mn, Cr, V,

25 G = at least one of the elements from Nb, Se, Te, Sm, Gd, La, Y, Pd, Pt, Ru, Ag, Au,

H = at least one of the elements from Si, Al, Ti, Zr,

a = 0 to 5.0,

b = 0.5 to 5.0,

30 c = 2 to 15,

d = 0.01 to 5.0,

e = 0.001 to 2,

f = 0.001 to 5,

g = 0 to 1.5,

35 h = 0 to 800,

x = number which is determined by the valency and frequency of the elements other than oxygen.

As already explained, one advantage of the process according to the invention is that, in the preparation of acrolein by catalytic gas phase oxidation of propylene, it is possible to employ propylene gas of lower quality without significantly worsening the performance characteristics of the oxidation catalyst used compared to the use of propylene of high quality. As described above, this is especially true of contamination by sulphur components and/or unsaturated hydrocarbons (C_2 - C_5), excluding C_3 .

However, the process according to the invention also allows the reaction gas provided to be produced by mixing at least refinery grade propylene and air, the refinery grade propylene being characterized in that it contains 0.05 to 2.0% by weight, preferably 0.1 to 1.0% by weight and further preferably 0.2 to 0.5% by weight of ethane and/or 9 to 40% by weight, preferably 10 to 35% by weight, further preferably 12 to 30% by weight, and especially preferably 15 to 25% by weight of propane.

The process according to the invention is preferably performed in such a way that, in step b), the reaction gas is passed through a reactor tube or through a plurality of bundled reactor tubes in parallel, the one or more reactor tubes each being filled with the oxidation catalyst to a length of at least 2 metres, preferably at least 2.5 metres, more preferably at least 3 metres. Typically, the reactor tubes are each charged with oxidation catalyst to a length of 1.5 to 5 metres, preferably 2 to 4.5 metres, more preferably 2.5 to 4 metres. The internal diameter of each reactor tube is in the range from 1.0 to 3.5 cm, preferably in the range from 1.5 to 3.3 cm, more preferably in the range from 2.0 to 3.0 cm.

In addition, the process according to the invention is preferably performed in such a way that, in step b),

the reaction gas is passed through the reactor tube or the plurality of reactor tubes in a bundle at a temperature in the range from 300 to 500°C, preferably in the range from 350 to 450°C, more preferably in the range from 370 to 430°C. The temperature can be set by controlling the temperature of the one or more reactor tube(s), for example by surrounding the one or more reactor tube(s) with a temperature-controlled heat carrier medium or by direct heating of the one or more reactor tube(s) with electrical heating elements.

It has been found that step b) of the process according to the invention can be operated over a period of 30 minutes to 2000 hours, preferably in the range from 1 to 1000 hours, more preferably in the range from 2 to 500 hours, without occurrence of any significant deterioration in the performance characteristics of the oxidation catalyst used; in this context, only the periods within which the reaction gas actually contains the amounts of sulphur components and/or unsaturated hydrocarbons specified in accordance with the invention are added up.

The present invention further provides for the use of a reaction gas for preparation of acrolein, characterized in that the reaction gas contains more than 10 ppm by weight of sulphur in the form of any sulphur components, the reaction gas in each case containing not more than 5000 ppm by weight, preferably not more than 1000 ppm by weight, of sulphur in the form of any sulphur components and not more than 5000 ppm by weight, preferably not more than 1500 ppm by weight, of unsaturated hydrocarbons, selected from the group consisting of C_2H_4 , C_3H_4 , C_4H_8 , C_4H_6 , C_5H_{10} , C_5H_8 and mixtures thereof.

The process according to the invention also allows more than 50 ppm by weight of unsaturated hydrocarbons

selected from the group consisting of C_2H_4 , C_3H_4 , C_4H_8 , C_4H_6 , C_5H_{10} , C_5H_8 and mixtures thereof to be present in the reaction gas provided.

5 The total content of sulphur in the form of any sulphur components and/or of unsaturated hydrocarbons, selected from the group consisting of C_2H_4 , C_3H_4 , C_4H_8 , C_4H_6 , C_5H_{10} , C_5H_8 and mixtures thereof, in the reaction gas may also be more than 20 ppm by weight in each case. More
10 particularly, the inventive use allows the total content of sulphur in the form of H_2S and/or SO_2 in the reaction gas to be more than 10 ppm by weight or else more than 20 ppm by weight, provided that the total content of sulphur in the form of any sulphur
15 components (including H_2S and/or SO_2) in the reaction gas is not more than 5000 ppm by weight, preferably not more than 1000 ppm by weight.

The present invention further also provides for the use
20 of an acrolein-containing gas mixture which is preparable by the process described above for preparation of acrylic acid.

In a preferred embodiment of the inventive use, the
25 preparation of acrylic acid comprises the mixing of the acrolein-containing gas mixture with further molecular oxygen and the contacting of the mixture with an oxidation catalyst to form an acrylic acid-containing gas mixture. This can be effected without purifying
30 removal of any sulphur present in the form of any sulphur components and of any unsaturated hydrocarbons selected from the group consisting of C_2H_4 , C_4H_8 , C_3H_4 , C_4H_6 , C_5H_{10} , C_5H_8 and mixtures thereof that are present.

35 Examples

Example 1

In a tubular reactor with 20 ml of catalyst bed, the heterogeneously catalysed partial oxidation of propylene was performed in the presence of molecular oxygen over a mixed metal oxide catalyst, the
5 preparation method for which can be found in DE 10 2006 015710 A1 (Example 1). As well as propylene and air, nitrogen (and optionally steam) was fed in as additional inert gas. The reactor was heated to about 360°C by means of an electrical oven. The temperature
10 in the catalyst bed was monitored by means of thermocouples, and the maximum temperature was about 400°C. The analysis of the process gas was performed by means of gas chromatography.

15 The reaction was first started up under standard conditions (= feed gas consisting of propylene, oxygen and inert gas, e.g. nitrogen). In order to study the influence of sulphur components, a mixture of sulphur component in inert gas (e.g. H₂S in nitrogen) was
20 metered in by means of an additional mass flow meter and replaces the inert gas of the standard conditions in a parallel stepwise manner, such that the total volume flow rate was kept constant. Results are given hereinafter according to various catalyst run times and
25 the respective proportion by mass of sulphur component (based on the overall gas stream):

Table 1: Catalyst performance after various run times with and without metered addition of H₂S.

Run time	Proportion by mass of H ₂ S [34 g/mol]	Proportion by mass of sulphur [32 g/mol]	H ₂ S metering time	Propylene conversion	Acrolein yield
[h]	[ppm by wt.]	[ppm by wt.]	[h]	[%]	[%]
50	0	0	-	90.1	80.0
135	0	0	-	90.6	80.0
315	220	207	150	91.6	80.1
550	435	409	337	89.9	80.0
810	870	819	260	90.0	80.6
1080	1500	1412	103	91.3	80.9

Example 2

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A bed of 2850 mm of catalyst was introduced into a tubular reactor of length 3400 mm with internal diameter of 21.7 mm. The reactor is surrounded by a heat carrier medium and thus kept at a constant temperature of 350°C. The reactor was charged with a reaction gas composed of propylene (9.3% by weight), air (58.3% by weight), remainder inert gas. Via a separate control path, SO₂ (as a pure substance and/or as a mixture with inert gas) was first metered in. The catalyst was run in and the metered addition of the sulphur component was commenced only after several days of steady-state operation. The proportion by mass was then increased gradually.

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Table 2: Catalyst performance after various run times without and with metered addition of SO₂ or H₂S.

Run time	Proportion by mass of SO ₂ [64 g/mol]	Proportion by mass of Sulphur [32 g/mol]	SO ₂ metering time	Propylene conversion	Acrolein yield
[h]	[ppm by wt.]	[ppm by wt.]	[h]	[%]	[%]
50	0	0	-	97.6	85.6
150	0	0	-	97.5	85.6
350	0	0	-	97.6	85.4
660	250	125	288	97.4	85.2
1000	1000	500	72	98.3	85.9
1200	2000	1000	120	98.7	85.9
1440	5000	2500	72	97.2	85.3
1670	10 000	5000	120	97.5	79.8
Regeneration					
Run time	Proportion by mass of SO ₂	Proportion by mass of Sulphur	SO ₂ metering time	Propylene conversion	Acrolein yield
[h]	[ppm by wt.]	[ppm by wt.]	[h]	[%]	[%]
1800	500	250	72	97.5	85.2
1950	1000	500	72	97.6	84.7

- 5 The results (conversion, yield) up to a catalyst run time of 350 h, in which no sulphur component was metered in, show the performance of the catalyst without involvement of sulphur components.
- 10 The run times reported in Tables 1 and 2 are gross run times. The period of H₂S or SO₂ metering with a particular proportion by mass of H₂S or SO₂ reported in each case took place within the period between the run times of H₂S or SO₂ metering with the next highest or
- 15 next lowest proportion by mass of H₂S or SO₂.

Example: The period of SO₂ metering of 288 h at a proportion by mass of SO₂ of 250 ppm by weight was within the interval between run time 350 and 1000 h.

For the rest of the interval, reaction gas was passed through the tubular reactor without SO₂ metering.

Claims

1. Process for preparing acrolein by catalytic gas phase oxidation, said process comprising the following steps:
 - a) providing a reaction gas comprising propylene and molecular oxygen, and
 - b) contacting the reaction gas with an oxidation catalyst to form a gas mixture comprising acrolein, the oxidation catalyst being a mixed oxide catalyst comprising or consisting of one or more base components selected from molybdenum, vanadium and tungsten, characterized in that more than 10 ppm by weight of sulphur in the form of any sulphur components is present in the reaction gas provided, but not more than 5000 ppm by weight of sulphur in the form of any sulphur components and not more than 5000 ppm by weight of unsaturated hydrocarbons selected from the group consisting of C_2H_4 , C_3H_4 , C_4H_8 , C_4H_6 , C_5H_{10} , C_5H_8 and mixtures thereof is present in each case in the reaction gas provided.
2. Process according to Claim 1, characterized in that more than 50 ppm by weight of unsaturated hydrocarbons selected from the group consisting of C_2H_4 , C_4H_8 , C_3H_4 , C_4H_6 , C_5H_{10} , C_5H_8 and mixtures thereof is present in the reaction gas provided.
3. Process according to either of the preceding claims, characterized in that more than 20 ppm by weight but not more than 1000 ppm by weight of sulphur in the form of any sulphur components is present in the reaction gas provided.
4. Process according to any of the preceding claims, characterized in that more than 20 ppm by weight of sulphur in the form of H_2S and/or SO_2 but not

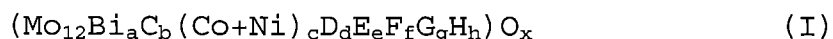
more than 1000 ppm by weight of sulphur in the form of any sulphur components is present in the reaction gas provided.

5 5. Process according to any of the preceding claims, characterized in that more than 100 ppm by weight but not more than 1500 ppm by weight of unsaturated hydrocarbons selected from the group consisting of C₂H₄, C₃H₄, C₄H₈, C₄H₆, C₅H₁₀, C₅H₈ and
10 mixtures thereof is present in the reaction gas provided.

6. Process according to any of the preceding claims, characterized in that more than 150 ppm by weight
15 but not more than 1300 ppm by weight of unsaturated hydrocarbons selected from the group consisting of C₂H₄, C₃H₄, C₄H₈, C₄H₆, C₅H₁₀, C₅H₈ and mixtures thereof is present in the reaction gas provided.

20 7. Process according to any of the preceding claims, characterized in that the mixed oxide catalyst additionally contains one or more additional components selected from bismuth, antimony, tellurium, tin, iron, cobalt, nickel and copper.
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8. Process according to Claim 7, characterized in that the oxidation catalyst is a mixed oxide catalyst of the general formula (I) or a mixture
30 of various mixed oxide catalysts of the general formula (I) where:



35 C = iron,
D = at least one of the elements from W, P,
E = at least one of the elements from Li, K, Na, Rb, Cs, Mg, Ca, Ba, Sr,

F = at least one of the elements from Ce, Mn, Cr, V,

G = at least one of the elements from Nb, Se, Te, Sm, Gd, La, Y, Pd, Pt, Ru, Ag, Au,

5 H = at least one of the elements from Si, Al, Ti, Zr,

a = 0 to 5.0,

b = 0.5 to 5.0,

c = 2 to 15,

10 d = 0.01 to 5.0,

e = 0.001 to 2,

f = 0.001 to 5,

g = 0 to 1.5,

h = 0 to 800,

15 x = number which is determined by the valency and frequency of the elements other than oxygen.

9. Process according to any of the preceding claims, wherein the reaction gas provided is produced by
20 mixing at least refinery grade propylene and air, the refinery grade propylene being characterized in that it contains 0.05 to 2.0% by weight of ethane and/or 9 to 40% by weight of propane.

25 10. Use of a reaction gas for preparation of acrolein, characterized in that the reaction gas contains more than 10 ppm by weight of sulphur in the form of any sulphur components, the reaction gas in each case containing not more than 5000 ppm by
30 weight of sulphur in the form of any sulphur components and not more than 5000 ppm by weight of unsaturated hydrocarbons, selected from the group consisting of C₂H₄, C₃H₄, C₄H₈, C₄H₆, C₅H₁₀, C₅H₈ and mixtures thereof.

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11. Use according to Claim 10, wherein the reaction gas contains more than 50 ppm by weight of unsaturated hydrocarbons selected from the group

consisting of C_2H_4 , C_3H_4 , C_4H_8 , C_4H_6 , C_5H_{10} , C_5H_8 and mixtures thereof.

12. Use of an acrolein-containing gas mixture prepared
5 by the process according to any of Claims 1 to 9
for preparation of acrylic acid.
13. Use according to Claim 12, wherein the acrolein-
containing gas mixture is mixed with further
10 molecular oxygen and contacted with an oxidation
catalyst to form an acrylic acid-containing gas
mixture.