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(54) Title: METHOD FOR PRODUCTION OF METHYL METHACRYLATE BY OXIDATIVE ESTERIFICATION USING A HETEROGENEOUS CATALYST

(57) **Abstract:** A method for preparing methyl methacrylate from methacrolein and methanol. The method comprises contacting a mixture comprising methacrolein, methanol and oxygen with a heterogeneous catalyst comprising a support and a noble metal, wherein oxygen concentration at a reactor outlet is from 1 to 7.5 mol% and wherein pH at a reactor outlet is no greater than 7.5.

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METHOD FOR PRODUCTION OF METHYL METHACRYLATE BY OXIDATIVE ESTERIFICATION USING A HETEROGENEOUS CATALYST

BACKGROUND OF THE INVENTION

The invention relates to a method for preparing methyl methacrylate from methacrolein and methanol using a heterogeneous catalyst.

Oxidative esterification of methacrolein to produce methyl methacrylate at relatively low pH are known, see, e.g., JP3408700(B2). However, this reference uses a palladium and lead catalyst and teaches that very low oxygen partial pressures are preferable. There is a need for methods that can provide improved selectivity in oxidative esterification reactions, especially with regard to the level of byproduct methyl isobutyrate.

SUMMARY OF THE INVENTION

The present invention is directed to a method for preparing methyl methacrylate from methacrolein and methanol; said method comprising contacting in a reactor a mixture comprising methacrolein, methanol and oxygen with a heterogeneous catalyst comprising a support and a noble metal, wherein oxygen concentration at a reactor outlet is from 1 to 7.5 mol% and wherein pH at a reactor outlet is no greater than 7.5.

DETAILED DESCRIPTION OF THE INVENTION

All percentage compositions are weight percentages (wt%), and all temperatures are in °C, unless otherwise indicated. A noble metal is any of gold, platinum, iridium, osmium, silver, palladium, rhodium and ruthenium. More than one noble metal may be present in the catalyst, in which case the limits apply to the total of all noble metals. The “catalyst center” is the centroid of the catalyst particle, i.e., the mean position of all points in all coordinate directions. A diameter is any linear dimension passing through the catalyst center and the average diameter is the arithmetic mean of all possible diameters. The aspect ratio is the ratio of the longest to the shortest diameters.

Preferably, the support is a particle of an oxide material; preferably γ-, δ-, or θ-alumina, silica, magnesia, titania, zirconia, hafnia, vanadia, niobium oxide, tantalum oxide, ceria, yttria, lanthanum oxide or a combination thereof; preferably γ-, δ-, or θ-alumina. Preferably, in portions of the catalyst comprising the noble metal, the support has a surface area greater than 10 m^2/g, preferably greater than 30 m^2/g, preferably greater than 50 m^2/g, preferably greater than 100 m^2/g, preferably greater than 120 m^2/g. . In portions of the catalyst which comprise little or no noble metal, the support may have a surface area less than 50 m^2/g, preferably less than 20 m^2/g.

Preferably, the aspect ratio of the catalyst particle is no more than 10:1, preferably no more than 5:1, preferably no more than 3:1, preferably no more than 2:1, preferably no more than 1.5:1, preferably no more than 1.1:1. Preferred shapes for the catalyst particle include spheres, cylinders, rectangular solids, rings, multi-lobed shapes (e.g., cloverleaf cross section), shapes having multiple holes and "wagon wheels;" preferably spheres. Irregular shapes may also be used.

Preferably, at least 90 wt% of the noble metal(s) is in the outer 70% of catalyst volume (i.e., the volume of an average catalyst particle), preferably the outer 60%, preferably the outer 50%, preferably the outer 40%, preferably the outer 35%, preferably in the outer 30%, preferably in the outer 25%. Preferably, the outer volume of any particle shape is calculated for a volume having a constant distance from its inner surface to its outer surface (the surface of the particle), measured along a line perpendicular to the outer surface. For example, for a spherical particle the outer x% of volume is a spherical shell whose outer surface is the surface of the particle and whose volume is x% of the volume of the entire sphere. Preferably, at least 95 wt% of the noble metal is in the outer volume of the catalyst, preferably at least 97 wt%, preferably at least 99 wt%. Preferably, at least 90 wt% (preferably at least 95 wt%, preferably at least 97 wt%, preferably at least 99 wt%) of the noble metal(s) is within a distance from the surface that is no more than 30% of the catalyst diameter, preferably no more than 25%, preferably no more than 20%, preferably no more than 15%, preferably no more than 10%, preferably no more than 8%. Distance from the surface is measured along a line which is perpendicular to the surface.

Preferably, the noble metal is gold or palladium, preferably gold. Preferably, the reaction mixture (including the catalyst) is substantially free of heavy metals that are not noble metals, e.g., lead, mercury, cadmium, chromium and manganese. Substantially free means having less than 500 ppm, preferably less than 100 ppm, preferably less than 50 ppm, preferably less than 20 ppm, preferably less than 10 ppm.

Preferably, the average diameter of the catalyst particle is at least 100 microns, preferably at least 200 microns, preferably at least 300 microns, preferably at least 400 microns, preferably at least 500 microns, preferably at least 600 microns, preferably at least 700 microns, preferably at least 800 microns; preferably no more than 30 mm, preferably no more than 20 mm, preferably no more than 10 mm, preferably no more than 7 mm, preferably no more than 5 mm. The average diameter of the support and the average diameter of the final catalyst particle are not significantly different.

Preferably, the amount of noble metal as a percentage of the noble metal and the support is from 0.2 to 5 wt%, preferably at least 0.5 wt%, preferably at least 0.8 wt%, preferably at least 1 wt%, preferably at least 1.2 wt%; preferably no more than 4 wt%, preferably no more than 3 wt%, preferably no more than 2.5 wt%.

Preferably, the catalyst is produced by precipitating the noble metal from an aqueous solution of noble metal salt in the presence of the support. In one embodiment of the invention, the catalyst is produced by incipient wetness in which an aqueous solution of a suitable noble metal precursor salt is added to a porous inorganic oxide such that the pores are filled with the solution and the water is then removed by drying. The resulting material is then converted into a finished catalyst by calcination, reduction, or other pre-treatments known to those skilled in the art to decompose the noble metal salts into metals or metal oxides. Preferably, a C_2-C_{18} thiol comprising at least one hydroxyl or carboxylic acid substituent is present in the solution. Preferably, the C_2-C_{18} thiol comprising at least one hydroxyl or carboxylic acid substituent has from 2 to 12 carbon atoms, preferably 2 to 8, preferably 3 to 6. Preferably, the thiol compound comprises no more than 4 total hydroxyl and carboxylic acid groups, preferably no more than 3, preferably no more than 2. Preferably, the thiol compound has no more than 2 thiol groups, preferably no more than one. If the thiol compound comprises carboxylic acid substituents, they may be present in the acid form, conjugate base form or a mixture thereof. Especially preferred thiol compounds include thiomalic acid, 3-mercaptopropionic acid, thioglycolic acid, 2-mercaptoethanol and 1-thioglycerol, including their conjugate bases.

In one embodiment of the invention, the catalyst is produced by deposition precipitation in which a porous inorganic oxide is immersed in an aqueous solution containing a suitable noble metal precursor salt and that salt is then made to interact with the surface of the inorganic oxide by adjusting the pH of the solution. The resulting treated solid is then recovered (e.g. by filtration) and then converted into a finished catalyst by calcination, reduction, or other pre-treatments known to those skilled in the art to decompose the noble metal salts into metals or metal oxides.

The process for producing methyl methacrylate (MMA) comprises treating methacrolein with methanol and oxygen in an oxidative esterification reactor (OER). Preferably, the catalyst particles are in a catalyst bed and preferably are held in place by solid walls and by screens or catalyst support grids. In some configurations, the screens or grids are on opposite ends of the catalyst bed and the solid walls are on the side(s), although in some configurations the catalyst bed may be enclosed entirely by screens. Preferred shapes for the catalyst bed include a cylinder, a rectangular solid and a cylindrical shell; preferably a cylinder. The liquid phase may further comprise byproducts, e.g., methacrolein dimethyl acetal (MDA) and methyl isobutyrate (MIB). MIB is a particularly problematic byproduct due to the difficulty in removing it and undesirable odor it creates. Preferably, the liquid phase is at a temperature from 40 to 120 °C; preferably at least 50 °C, preferably at least 60 °C; preferably no more than 110 °C, preferably no more than 100 °C. Preferably, the catalyst bed is at a pressure from 0 to 2000 psig (101.3 to 13890.8 kPa); preferably no more than 2000 kPa, preferably no more than 1500 kPa. Preferably, the catalyst bed is in a tubular continuous reactor comprising axial flow of liquid and gaseous reactants; preferably the tubular reactor has a circular cross-section. Preferably, the catalyst bed further comprises oxygen gas.

The OER typically produces MMA, along with methacrylic acid and unreacted methanol. Preferably, methanol and methacrolein are fed to the reactor containing the catalyst bed in a methanol:methacrolein molar ratio from 1:10 to 100:1, preferably from 1:2 to 20:1, preferably from 1:1 to 10:1. Preferably, the catalyst bed further comprises inert materials located below and/or above the catalyst. Preferred inert materials include, e.g., alumina, clay, glass, silica carbide and quartz. Preferably the inert material has an average diameter equal to or larger than that of the catalyst. Preferably, the reaction products are fed to a methanol recovery distillation column which provides an overhead stream rich in methanol and methacrolein; preferably this stream is recycled back to the OER. The bottoms stream from the methanol recovery distillation column comprises MMA, MDA, methacrylic acid, salts and water. In one embodiment of the invention, MDA is hydrolyzed in a medium comprising MMA, MDA, methacrylic acid and water. In another embodiment, MDA is hydrolyzed in an organic phase separated from the bottoms stream of a methanol recovery distillation column. It may be necessary to add water to the organic phase to ensure that there is sufficient water for the MDA hydrolysis; these amounts may be determined easily from the composition of the organic phase. The product of the MDA hydrolysis reactor is phase separated and the organic phase passes through one or more distillation columns to produce MMA product and light and/or heavy byproducts. In another embodiment, hydrolysis could be conducted within the distillation column itself.

One preferred embodiment is a recycle reactor with cooling capacity in the recycle loop. Another preferred embodiment is a series of reactors with cooling and mixing capacity between the reactors.

Preferably, oxygen concentration at a reactor outlet is at least 1.4 mol%, preferably at least 1.6 mol%, preferably at least 1.8 mol%, preferably at least 2.0 mol%, preferably at least 2.2 mol%; preferably no more than 7 mol%, preferably no more than 6.5 mol%, preferably no more than 6 mol%, preferably no more than 5.5 mol%. Preferably, the superficial velocity of liquid through the reactor is from 1 to 50 mm/s, preferably at least 2 mm/s, preferably at least 3 mm/s, preferably at least 4 mm/s, preferably at least 5 mm/s; preferably no more than 40 mm/s, preferably no more than 25 mm/s.

In a preferred embodiment of the invention, pH at the reactor outlet is at least 3, preferably at least 3.5, preferably at least 4, preferably at least 4.5, preferably at least 5; preferably no more than 7.2, preferably no more than 7, preferably no more than 6.8, preferably no more than 6.7, preferably no more than 6.6, preferably no more than 6.5. Preferably, base is not added to the reactor or to liquid streams entering the reactor. Preferably, the reactor is not connected to an external mixing tank through which base is introduced. pH in the reactor is likely to be higher near the inlet, possibly above 7, and to drop steadily moving towards the outlet.

One preferred embodiment of the fixed bed reactor for oxidative esterification is a trickle bed reactor, which contains a fixed bed of catalyst and passes both the gas and liquid feeds through the reactor in the downward direction. In trickle flow, the gas phase is the continuous fluid phase. Thus, the zone at the top of the reactor, above the fixed bed, will be filled with a vapor phase mixture of nitrogen, oxygen, and the volatile liquid components at their respective vapor pressures. Under typical operating temperatures and pressures (50-90°C and 60-300 psig), this vapor mixture is inside the flammable envelope if the gas feed is air. Thus, only an ignition source would be required to initiate a deflagration, which could lead to loss of primary containment and harm to the physical infrastructure and personnel in the vicinity. In order to address process safety considerations, a means to operate a trickle bed reactor while avoiding a flammable headspace atmosphere is operation with a gas feed containing a sufficiently low oxygen mole fraction to ensure the oxygen concentration in the vapor headspace is below the limiting oxygen concentration (LOC). Knowledge of the LOC is required for the fuel mixture, temperature, and pressure of concern. Since the LOC decreases with increasing temperature and pressure, and given that methanol gives a lower LOC than the other two significant fuels (methacrolein and methyl methacrylate), a conservative design chooses a feed oxygen to nitrogen ratio that ensures a composition with less than the LOC at the highest expected operating temperature and pressure. For example, for a reactor operated at up to 100°C and 275 psig, the feed oxygen concentration in nitrogen should not exceed 7.4 mol%.

EXAMPLES

Examples of the effect of vent O_2 concentration and pH are provided below.

Example 1

A series of runs was conducted in which 20 wt% methacrolein, 200 ppm inhibitor, and a balance of methanol were fed to a 3/8” (9.5 mm) stainless steel tubular reactor containing a short front section of silica carbide followed by 10 g of catalyst. The catalyst consisted of 1.5 wt% Au on a NORPRO 1mm diameter high surface area alumina spherical support. A gas containing 8% oxygen in nitrogen was also feed to the reactor in all cases except where denoted otherwise (**) in which case air was fed to the reactor. The reactor was operated at 60 °C and 160 psig (1205 kPa). The product of the reactor was sent to a liquid-vapor separator and the vapor was sent to a condenser with liquid return. A portion of the product stream from this separator was recycled in some cases to the reactor inlet and combined with the feed entering the reactor. Results are described in the below table. MIB is reported in ppm on a 100% MMA product basis. Percent MMA in the products formed from methacrolein for all runs exceeded 95 wt%.

Table 1. Effect of Mole % Oxygen at Reactor Outlet and pH on MIB Formation*

MIB (ppm)	Base (g/hr)	Feed (g/hr)	Recycle (g/hr)	Base Type	pH (outlet)	Liq. Vel. (mm/s)	Gas Flow (sccm)	Avg. P_{O2} (kPa)	Vent O_2, mole%
670	0	200	0	None	6.3	1.35	200	59.6	1.9
540	0	100	100	None	6.3	1.35	200	62.1	2.3
540	0	200	0	None	6.3	1.35	500	63.8	2.6
470	0	100	100	None	6.3	1.35	500	66.9	3.1
480	0	20	180	None	5.7	1.35	380	72.3	4
1170	0	100	0	None	6.8	0.67	75	49.4	0.2
910	4	40	50	3wt% NaOMe	8.0	0.64	80**	153.5	4.5

* Liquid velocity (Liq. Vel.) is the superficial liquid velocity and average partial pressure oxygen (Avg. P_{O2}) is in kPa absolute. Average partial pressure is the arithmetic average of inlet and outlet oxygen partial pressures.

** air was used in this case instead of 8% O_2

CLAIMS:

1. A method for preparing methyl methacrylate from methacrolein and methanol; said method comprising contacting in a reactor a mixture comprising methacrolein, methanol and oxygen with a heterogeneous catalyst comprising a support and a noble metal, wherein oxygen concentration at a reactor outlet is from 1 to 7.5 mol% and wherein pH at a reactor outlet is no greater than 7.5.

2. The method of claim 1 in which the reactor is an axial flow reactor having a liquid-phase superficial velocity of 0.5 to 20 mm/s and an average partial pressure of oxygen greater than 50kPa.

3. The method of claim 2 in which the catalyst has an average diameter from 400 microns to 10 mm.

4. The method of claim 3 in which the catalyst is contained in a catalyst bed which is at a temperature from 40 to 120 °C.

5. The method of claim 4 in which pH in the reactor is from 3 to 7.2.

6. The method of claim 5 in which oxygen concentration at a reactor outlet is from 1.6 to 6 mol%.

7. The method of claim 6 in which the noble metal is selected from the group consisting of gold and palladium.

8. The method of claim 7 in which the support is selected from the group consisting of γ-, δ-, or θ-alumina, silica, magnesia, titania, zirconia, hafnia, vanadia, niobium oxide, tantalum oxide, ceria, yttria, lanthanum oxide and combinations thereof.

9. The method of claim 8 in which methanol and methacrolein are fed to a reactor containing the catalyst bed in a molar ratio from 1:1 to 10:1, respectively.

10. The method of claim 9 in which at least 90 wt% of the noble metal is in the outer 70% of catalyst volume.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C67/39 C07C69/54 B01J23/44 B01J23/52
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

Date of the actual completion of the international search 26 November 2018	Date of mailing of the international search report 07/12/2018
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Patteux, Claudine

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International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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