

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

BACKGROUND OF THE INVENTION

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

 The use of fixed bed reactors and, in particular, the use of trickle bed reactors for oxidative esterification reactions is known, see e.g. US4518796. However, there is a need for an improved process which provides for safe operation.

10 **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 said catalyst has an average diameter of at least 200
15 microns, liquid and gaseous reactants flow downward in the reactor and wherein the continuous phase in the reactor is a gas which has no more than 7.5 mol% oxygen at reactor inlets.

DETAILED DESCRIPTION OF THE INVENTION

 All percentage compositions are weight percentages (wt%), and all temperatures are
20 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
25 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.
30 Preferably, in portions of the catalyst comprising the noble metal, the support has a surface area greater than 10 m²/g, preferably greater than 30 m²/g, preferably greater than 50 m²/g, preferably greater than 100 m²/g, preferably greater than 120 m²/g. . In portions of the catalyst which comprise little or no noble metal, the support may have a surface area less than 50 m²/g, preferably less than 20 m²/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 in 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 average diameter of the catalyst particle is 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 5 mm, preferably no more than 4 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 C₂-C₁₈ thiol comprising at least one hydroxyl or carboxylic acid substituent is present in the solution. Preferably, the C₂-C₁₈ 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-mercaptoproethanol 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). 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 or a continuous stirred tank reactor.

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 above and/or below 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, salts and water. MDA may be hydrolyzed in the bottoms stream from a methanol recovery distillation column; said stream comprising MMA, MDA, methacrylic acid, salts and water. In another embodiment, MDA is hydrolyzed in an organic phase separated from the methanol recovery bottoms stream. 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.

Preferably, oxygen concentration is no greater than 7 mol% at inlets to the reactor (i.e., any incoming gas stream comprises no more than 7 mol% oxygen), preferably no greater than 6.5 mol%, preferably no greater than 6 mol%; preferably at least 3 mol%, preferably at least 3.5 mol%, preferably at least 4 mol%. The incoming gas stream comprises oxygen and inert diluent(s); preferably the diluent(s) comprise at least one of nitrogen and carbon dioxide, preferably nitrogen. Preferably, the incoming gas stream is air diluted with inert diluent(s) (i.e., gases having a lower level of oxygen than air). Preferably, offgas from the reactor is recycled and used to dilute the incoming gas stream. Preferably, offgas is removed from the reactor and sent to a condenser, methanol scrubber, or other device to remove volatile organic compounds prior to releasing the non-condensable gases to the atmosphere. 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 30 mm/s, preferably no more than 20 mm/s.

In a preferred embodiment of the invention, pH at the reactor outlet is from 3 to 6.7; preferably at least 3.5, preferably at least 4, preferably at least 4.5, preferably at least 4.8, preferably at least 5; preferably no more than 6.6, preferably no more than 6.5, preferably no more than 6.4, preferably no more than 6.3, preferably no more than 6.2. 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.

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, carbon dioxide (or other inert gas) 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 inert gas 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 should not exceed 7.4 mol% in nitrogen, carbon dioxide, or other inert gas (molar basis). In order to reduce the concentration of oxygen entering the reactor, air may be mixed with an inert gas such as nitrogen, carbon dioxide, or other inert. In the present invention, the concept is to recycle the off-gas of the reactor and add just enough air to that stream in order to bring the oxygen content up to a safe level, typically less than 7.5 mol%. The off-gas of an OER is typically

sent to a condenser, methanol scrubber, or other device in order to remove the volatile organics before the non-condensable gases are released to the atmosphere. The recycle gas stream which would be sent back to the OER would be taken from the OER off-gases either before or after the removal of volatile organics. Preferably, the gas recycle would be taken
5 from the OER off-gas stream before the volatile organics were removed by condenser, methanol scrubber or other such device and before the pressure of that stream is reduced. These gases, which would still be at approximately the pressure of the OER, would be sent to the entrance of the OER and mixed with air prior to being fed to the OER. The gases entering the OER would preferably be between 6 mol% and 7.5 mol% oxygen and the gases
10 exiting the OER would typically be between 0.5 mol% oxygen and 6 mol% oxygen.

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.

EXAMPLES

EXAMPLE 1 Trickle Bed Reactor

A series of experiments were conducted in a ¼” 316 stainless steel tube reactor that was housed within a ½” jacket (6.4 mm tube, 12.7 mm jacket). The jacket was fed with water from a heating bath. The liquid stream was fed via a pump at a nominal design rate of 0.1 mL/min. The gas phase reactant is oxygen, which was fed either as air or a diluted air stream in helium. The air and helium flow rates were controlled via mass flow controllers. Typical operating pressures ranged from 60 psig to 170 psig (510 to 1270 kPa). The gas streams were pre-mixed prior to being mixed with the liquid feed preceding the reactor.

This series of experiments were operated in down-flow trickle-bed mode.

The reactor catalyst was loaded with 0.4 g of 1 wt% Au on 1 mm x 5 mm alumina extrudates (non-eggshell catalyst). The extrudates were diluted with ~20 g of 200 micron SiC fines.

T (°C)	P (psig)	Air (sccm)	He (sccm)	O ₂ in Gas At Inlet	O ₂ in Gas At Outlet	Liquid Flow (g/min)	MA wt%	STY (mol/kg/hr)	MA Conv (%)	MMA Distribution (%)
60	160	6.1	0	0.21	0.12	0.110	10	8.5	40	98
60	160	23	23	0.11	0.09	0.110	10	7.0	30	97
60	160	20	50	0.06	0.05	0.110	10	5.0	20	96
60	160	20	50	0.06	0.05	0.055	10	4.5	40	96

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EXAMPLE 2 Trickle Bed Reactor

A series of experiments were conducted in a ¼” 316 stainless steel tube reactor that was housed within a ½” jacket. The jacket was fed with water from a heating bath. The liquid stream was fed via a pump at a nominal design rate of 0.1 mL/min. The gas phase reactant is oxygen, which was fed either as air or a diluted air stream in helium. The air and helium flow rates were controlled via mass flow controllers. Typical operating pressures ranged from 60 psig to 170 psig. The gas streams were pre-mixed prior to being mixed with the liquid feed preceding the reactor. This series of experiments were operated in down-flow trickle-bed mode.

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The reactor catalyst was loaded with 0.5 g of 1.2 wt% Au on 1/16-inch alumina extrudates (eggshell catalyst). The extrudates were diluted with ~20 g of 200 micron SiC fines.

T (°C)	P (psig)	Air (sccm)	He (sccm)	O ₂ in Gas At Inlet	Liquid Flow (g/min)	MA wt%	STY (mol/kg/hr)	MA Conv (%)	MMA Distribution (%)
60	160	20	50	0.06	0.055	10	6.0	50	98
60	160	20	0	0.21	0.055	10	10.5	80	98

EXAMPLE 3 Trickle Bed Reactor

A series of experiments were conducted in a ¼" 316 stainless steel tube reactor that was housed within a ½" jacket. The jacket was fed with water from a heating bath. The liquid stream was fed via a pump at a nominal design rate of 0.1 mL/min. The gas phase reactant is oxygen, which was fed either as air or a diluted air stream in helium. The air and helium flow rates were controlled via mass flow controllers. Typical operating pressures ranged from 60 psig to 170 psig. The gas streams were pre-mixed prior to being mixed with the liquid feed preceding the reactor. This series of experiments were operated in down-flow trickle-bed mode.

The reactor catalyst was loaded with 0.5 g of 1.5 wt% Au on 1 mm alumina spheres (eggshell catalyst). The extrudates were diluted with ~20 g of 200 micron SiC fines.

T (°C)	P (psig)	Air (sccm)	He (sccm)	O ₂ in Gas At Inlet	Liquid Flow (g/min)	MA wt%	STY (mol/kg/hr)	MA Conv (%)	MMA Distribution (%)
60	160	20	50	0.06	0.055	10	4.5	40	97
60	160	20	0	0.21	0.055	10	7.0	60	97

EXAMPLE 4 COMPARATIVE EXAMPLE OF BUBBLE COLUMN REACTOR

A series of experiments were conducted in a ¼" 316 stainless steel tube reactor that was housed within a ½" jacket. The jacket was fed with water from a heating bath. The liquid stream was fed via a pump at a nominal design rate of 0.1 mL/min. The gas phase reactant is oxygen, which was fed either as air or a diluted air stream in helium. The air and helium flow rates were controlled via mass flow controllers. Typical operating pressures ranged from 60 psig to 170 psig. The gas streams were pre-mixed prior to being mixed with the liquid feed preceding the reactor. This series of experiments were operated in up-flow as a bubble column reactor.

The reactor catalyst was loaded with 0.4 g of 1 wt% Au on 1 mm x 5 mm alumina extrudates (non-eggshell catalyst). The extrudates were diluted with ~20 g of 200 micron SiC fines.

T (°C)	P (psig)	Air (sccm)	He (sccm)	O ₂ in Gas At Inlet	O ₂ in Gas At Outlet	Liquid Flow (g/min)	MA wt%	STY (mol/kg/hr)	MA Conv (%)	MMA Distribution (%)
60	160	20	50	0.06	0.05	0.055	10	4.5	35	98
60	160	2.0	0	0.21	0.06	0.055	10	6.0	50	96

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CONCLUSIONS FROM DATA: The conclusion of these studies is that operation with 6mol% O₂ in down-flow trickle bed mode is comparable or better than operation in up-flow bubble column mode. Although performance is not as good as with 21% O₂ in the feed, safety concerns make this mode of operation preferable.

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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 said catalyst has an average diameter of at least 200 microns, liquid and gaseous reactants flow downward in the reactor and wherein the continuous phase in the reactor is a gas which has no more than 7.5 mol% oxygen at reactor inlets, and wherein base is not added to the reactor or to liquid streams entering the reactor.
2. The method of claim 1 in which the catalyst has an average diameter from 400 microns to 10 mm.
3. The method of claim 2 in which the catalyst is contained in a catalyst bed.
4. The method of claim 3 in which the catalyst bed is at a temperature from 40 to 120 °C and pH in the catalyst bed is from 4 to 10.
5. The method of claim 4 in which offgas from the reactor is recycled and combined with air or oxygen.
6. The method of claim 5 in which at least 90 wt% of the noble metal is in the outer 70% of catalyst volume.
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.
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 95 wt% of the noble metal is in the outer 40% of catalyst volume.