

HETEROGENEOUS CATALYST

BACKGROUND OF THE INVENTION

The invention relates to a heterogeneous catalyst. The catalyst is especially useful in
5 a process for preparing methyl methacrylate from methacrolein and methanol.

Heterogeneous catalysts having noble metals concentrated in an outer region of the catalyst are known, see, e.g., U.S. Pat. No. 6,228,800. However, there is a need for larger catalyst particles with noble metals more highly concentrated near the surface.

SUMMARY OF THE INVENTION

10 The present invention is directed to a heterogeneous catalyst comprising a support and a noble metal, wherein said catalyst has an average diameter of at least 200 microns and at least 90 wt% of the noble metal is in the outer 50% of catalyst volume.

The present invention is further directed to a catalyst bed comprising the catalyst.

DETAILED DESCRIPTION OF THE INVENTION

15 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
20 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 a refractory oxide; preferably γ -, δ -, or θ -alumina, silica, magnesia, titania, zirconia, hafnia, vanadia, niobium oxide, tantalum oxide,
25 ceria, yttria, lanthanum oxide or a combination thereof; preferably γ -, δ -, or θ -alumina. Preferably, in portions of the catalyst comprising 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 with
30 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 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 40% of catalyst volume (i.e., the volume of an average catalyst particle), preferably the outer 35%,
5 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
10 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 15% of the catalyst diameter, preferably no more than 10%, preferably no
15 more than 8%, preferably no more than 6%. 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
20 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
25 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%.

The catalyst of this invention is useful in a process for producing methyl methacrylate (MMA) which comprises treating methacrolein with methanol in an oxidative
30 esterification reactor (OER) containing a catalyst bed. The catalyst bed comprises the catalyst particles and is situated within the OER that liquid flow may occur through the catalyst bed. The catalyst particles in the catalyst bed typically are held in place by solid walls and by screens. In some configurations, the screens 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 OER further comprises a liquid phase comprising methacrolein, methanol and MMA and a gaseous phase comprising oxygen. The liquid phase may further comprise byproducts, e.g.,
5 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 kPa to 14 MPa); preferably no more than 2000 kPa, preferably no more than 1500 kPa. Preferably, pH in the catalyst bed is
10 from 4 to 10; preferably at least 4.5, preferably at least 5; preferably no greater than 9, preferably no greater than 8, preferably no greater than 7.5, preferably no greater than 7, preferably no greater than 6.5. Preferably, the catalyst bed is in a tubular continuous reactor or a continuous stirred tank reactor.

Preferably, the catalyst is produced by precipitating the noble metal from an aqueous
15 solution of metal salts in the presence of the support. Preferred noble metal salts include tetrachloroauric acid, sodium aurothiosulfate, sodium aurothiomalate, gold hydroxide, palladium nitrate, palladium chloride and palladium acetate. In one preferred embodiment, the catalyst is produced by an incipient wetness technique in which an aqueous solution of a suitable noble metal precursor salt is added to a porous inorganic oxide such that the pores
20 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 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
25 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
30 the acid form, conjugate base form or a mixture thereof. The thiol component also may be present either in its thiol (acid) form or its conjugate base (thiolate) form. Especially preferred thiol compounds include thiomalic acid, 3-mercaptopropionic acid, thioglycolic acid, 2-mercaptoethanol and 1-thioglycerol, including their conjugate bases.

In another preferred embodiment, 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
5 solid is then recovered (e.g. by filtration) and then converted into a finished catalyst by calcination, reduction, or other treatments known to those skilled in the art to decompose the noble metal salts into metals or metal oxides.

EXAMPLES

Catalyst 778: "Egg Shell" Gold Catalyst

0.3088 g of sodium aurothiomalate was dissolved in 8.908 g of DI water with stirring. Next,
 5 10.0243 g of alumina (3.2 mm spheres, Norpro SA6275, Lot No. 2016910048) which had
 previously been stored in a drying oven at 120 °C were placed in a ceramic crucible. The
 aqueous gold salt was added drop-wise with periodic stirring using a spatula until the incipient
 wetness point of the support was reached.

The resulting material was dried for 1 hour at 120 °C and then calcined in a muffle furnace at
 10 300 °C (5 °C/min ramp) for 4 hours. The resulting purple catalyst spheres were then stored
 in an amber vial until ready for use. Elemental analysis via NAA revealed the following
 elemental composition:

Description	Au, wt%	Na, ppm	Cl, ppm
Catalyst 778	1.38 ± 0.05	1000 ± 30	340 ± 20

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Catalyst 780: Uniform Gold Catalyst (Comparative)

0.3918 g of sodium aurothiosulfate hydrate was dissolved in 9.0567 g of DI water. A
 10.0368 g sample of alumina (3.2 mm spheres, Norpro SA6275, Lot No. 2016910048)
 which had previously been stored in a drying oven at 120 °C was placed in a ceramic
 20 crucible. The aqueous gold salt was added drop-wise with periodic stirring using a spatula
 until the incipient wetness point of the support was reached.

The resulting material was dried for 1 hour at 120 °C and then calcined in a muffle furnace
 at 300 °C (5 °C/min ramp) for 4 hours. The resulting purple catalyst spheres were then
 stored in an amber vial until ready for use. Elemental analysis via NAA revealed the
 25 following elemental composition:

Catalyst ID	Description	Au Precursor	Calcination Temp (°C)	Calcination Time (hrs)
778	1.5wt% Au, 3.2mm Al ₂ O ₃	sodium aurothiomalate (I)	300	4
780	1.5wt% Au, 3.2 mm Al ₂ O ₃	gold (I) sodium thiosulfate hydrate	400	4

EDS scans of the catalysts were done with the following results.

Catalyst 780 (comparative)

wt% Au	Distance in microns from outer edge of the catalyst	Volume % of the catalyst
95	750	85%
90	680	81%

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The data for Catalyst 780 show that 90 wt% of the gold is within 680 microns of the outer edge, corresponding to the outer 81% of catalyst volume; and that 95 wt% is within 750 microns, or the outer 85%.

10 Catalyst 778

wt% Au	Distance in microns from outer edge of the catalyst	Volume % of the catalyst
95	75	13.4%
90	70	12.6%

The data for Catalyst 778 (“egg-shell”) show that 90 wt% of the gold is within 70 microns of the outer edge, corresponding to the outer 12.6% of catalyst volume; and that 95 wt% is within 75 microns, or the outer 13.4%.

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Catalyst Testing

Catalysts were evaluated in a continuous fixed-bed reactor operated in trickle flow mode. In each case, approximately 0.5 g of catalyst was mixed with silicon carbide grit to ensure uniform wetting. The catalyst bed was sandwiched between layers of glass beads. The reactor was operated at 60 °C and 160 psig (1200 kPa) with an inlet oxygen composition of 6 (achieved with 20 sccm air and 50 sccm He) or 21 mol% O₂ at a gas flow rate of 70 sccm. Liquid feed (10 wt% methacrolein in methanol) was introduced at a flow rate of 0.07 mL/min. Performance over time, MMA rate as a space time yield, and MIB content (ppm on a 100% MMA basis) are shown in the table below.

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	Oxygen level fed to reactor [mol%]	Space-Time Yield [mol MMA/kgcat/hr]	Product MIB on a 100% MMA basis [ppm]
“Egg-shell” metal loading (#778)	6	4	504
	21	4	423
Predominately uniform metal loading (#780) (comparative)	6	1	740
	21	2	405

- The data show that at high oxygen levels formation of byproduct MIB is low. However, at low oxygen levels, such as those that exist towards the end of a catalyst bed where the oxygen is depleted, the inventive “egg-shell” catalyst provides a greatly reduced level of
- 5 MIB. The space-time yield for the inventive catalyst is superior at both oxygen levels, but especially at low oxygen level.

CLAIMS:

1. A heterogeneous catalyst comprising a support and a noble metal, wherein said catalyst has an average diameter of at least 200 microns and at least 90 wt% of the noble metal is in the outer 50% of catalyst volume, wherein the catalyst is produced by precipitating the noble metal from an aqueous solution of metal salts in the presence of the support, and wherein a C₂-C₁₈ thiol comprising at least one hydroxyl or carboxylic acid substituent is present in the aqueous solution, and
wherein the noble metal is gold.
2. The catalyst of claim 1 in which the catalyst has an average diameter from 400 microns to 10 mm.
3. The catalyst of claim 2 in which at least 90 wt% of the noble metal is in the outer 35% of catalyst volume.
4. The catalyst of claim 3 in which the support is selected from the group consisting of γ -, δ -, or θ -alumina, silica, magnesia, titania, vanadia, ceria, lanthanum oxide and a combination thereof.
5. The catalyst of claim 4 in which the catalyst has a ratio of the longest to the shortest diameter of no more than 3:1.
6. A catalyst bed which comprises (i) a heterogeneous catalyst, wherein said catalyst comprises a support and a noble metal, and wherein said catalyst has an average diameter of at least 200 microns and at least 90 wt% of the noble metal is in the outer 50% of catalyst volume, wherein the catalyst is produced by precipitating the noble metal from an aqueous solution of metal salts in the presence of the support, and wherein a C₂-C₁₈ thiol comprising at least one hydroxyl or carboxylic acid substituent is present in the aqueous solution, and
wherein the noble metal is gold.
7. The catalyst bed of claim 6 in which the catalyst has an average diameter from 400 microns to 10 mm and the catalyst bed further comprises a gaseous phase comprising oxygen.

8. The catalyst bed of claim 7 in which at least 90 wt% of the noble metal is in the outer 40% of catalyst volume.