

OXIDATION CATALYST

BACKGROUND OF THE INVENTION

This invention relates to a catalyst.

PCT/GB 94/00321 discloses a catalyst for use in the oxidation of carbon monoxide and hydrocarbons which comprises a porous alumina support having captured thereon a complex comprising gold, a transition metal selected from cobalt and manganese, and the alumina, the concentration of gold on the support being less than 2 percent by mass of the catalyst, and the atomic ratio of gold to transition metal being in the range 1:30 to 1:200. Of these catalysts, the preferred catalyst is one which has cobalt as the transition metal. The alumina is said to have a large surface area, typically 80 to 400m²/g.

PCT/GB 95/02566 discloses a catalyst comprising an oxide support selected from zirconium oxide, cerium oxide and mixtures thereof having captured thereon a noble metal in catalytically effective form. Preferably the noble metal is gold and there is also present a transition metal oxide having a spinel structure, e.g. cobalt oxide or ferric oxide, with the gold being associated with the transition metal oxide. This catalyst is also suitable for catalysing the oxidation of carbon monoxide and hydrocarbons and also reducing hazardous nitrous oxides

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SUMMARY OF THE INVENTION

A catalyst for use in catalysing the oxidation of carbon monoxide and hydrocarbons which comprises an oxide support having captured thereon a noble metal in catalytically effective form, is characterised by the presence of an oxide of titanium, molybdenum or a mixture thereof. The presence of the oxide of titanium or molybdenum or a mixture thereof has the effect of stabilising the catalyst in the presence of sulphur, particularly sulphur dioxide, and thereby significantly improving the sulphur tolerance of the catalyst, particularly at low temperature.

Further according to the invention, a method of oxidising carbon monoxide or a hydrocarbon in the presence of sulphur includes the step of catalysing the oxidation using a catalyst as described above.

DESCRIPTION OF EMBODIMENTS

The oxide of titanium or molybdenum or mixtures thereof will typically be provided in an amount of up to about 15 percent, generally up to about 10 percent, by mass of the catalyst. The oxide will generally be provided in finely particulate form and have a large surface area, e.g. have a surface area of the order of 80 to 200m²/g.

In the catalyst of the invention, the oxide of titanium and/or molybdenum may be produced *in situ*, i.e. the metal included in the catalyst which is converted to oxide form during formation or on activation of the catalyst, or it may be added to the support oxide, as the oxide.

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The catalyst is preferably one wherein the oxide support is zirconium oxide, cerium oxide or a mixture thereof present in the catalyst in an amount of at least 50 percent by mass of the catalyst. When the support comprises a mixture of these two oxides, the cerium oxide will generally constitute at least 50 percent by mass of the mixture. The oxide support may also be other types of oxide, e.g. alumina.

The noble metal will generally be gold, platinum, palladium, rhodium or silver, with gold being the preferred noble metal.

The concentration of the noble metal will generally be low, i.e. less than 2 percent by mass of the catalyst. Preferably the noble metal concentration is of the order of 0,1 to 0,5 percent by mass of the catalyst.

The catalyst preferably also contains a transition metal in oxide form. The transition metal oxide preferably has a spinel structure. Examples of transition metal oxides which form spinel structures are cobalt oxide (Co_3O_4) and ferric oxide (Fe_3O_4).

When the noble metal is gold, the preferred catalyst also contains a transition metal oxide having a spinel structure and to which the gold is associated, e.g. complexed.

The oxide support will be porous and able to capture as much of the noble metal/transition metal oxide thereon as possible. The oxide support should have as large a surface area as possible, typically 80 to 200m²/g. The oxide support may take any suitable form such as a monolith, an extrudate, pellets, rings, pearls or preferably a powder.

The ratio of noble metal to transition metal, when present, in the catalyst, can vary over a wide range. Generally, the atomic ratio of noble metal to the transition metal will not exceed 1:100.

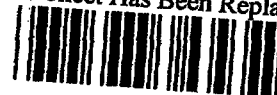
The catalyst, when it contains both a noble metal and a transition metal oxide, may be made by the method described in PCT/GB 95/00136. The method involves impregnating the oxide support with a solution of the transition metal, optionally drying the product, exposing the impregnated product to a reducing atmosphere such as hydrogen or carbon monoxide at a temperature exceeding 300°C, impregnating the thus treated product with a solution of the noble metal and drying the impregnated product. The catalyst may be activated by exposing it to a temperature of at least 300°C, typically 300 to 700°C, in the presence of oxygen. The oxygen may be air or oxygen mixed with another gas.

The invention will now be illustrated by the following examples.

EXAMPLE 1

A catalyst was produced using the method generally disclosed in PCT/GB 95/00136 and comprised 0,5% gold, 9,5% cobalt, 80% zirconium oxide/cerium oxide and 10% titanium dioxide, all percentages being by mass. The cobalt was in the form of cobalt oxide having a spinel structure, and the gold was in association, i.e. complexed, with the cobalt oxide spinel. In producing the catalyst, the titanium dioxide was added as the oxide to the catalyst.

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The catalytic effectiveness of the catalyst in the oxidation of carbon monoxide and hydrocarbons (HC) was tested at various temperatures and the results thereof are set out in Table 1.

TABLE 1
Effect of TiO₂ on Catalytic Activity

Temperature °C	Conversion (%)									
	Rt°		200°		300°		400°		500°	
	CO	HC	CO	HC	CO	HC	CO	HC	CO	HC
Sample 1 (with TiO ₂)	78	53	92	22	100	78	100	95	100	96
Sample 2 (with TiO ₂)	89	58	100	38	100	79	100	98	100	98
Sample 3 (without)	50	39	72	12	98	70	100	87	100	95
Sample 4 (without)	57	44	77	18	100	72	100	88	100	96

Test conditions: steady state
 Space velocity: 60 000 h
 Gas composition: 1% CO, 0,9% O₂, 700 ppm HC, 2% moisture, 15 ppm SO₂, balance N₂.

The beneficial effect of TiO₂ presence in the catalytic composition is most noticeable at lower temperatures.

EXAMPLE 2

A catalyst was produced using the method generally described in PCT/GB 95/00136 and comprised 0,5% gold, 9,5% cobalt, 80% zirconium oxide/cerium oxide, 9,5% titanium dioxide and 0,5% molybdenum oxide, all percentages being by mass. The cobalt was in the form of cobalt oxide having a spinel structure, and the gold was in association, i.e. complexed,

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with the cobalt oxide spinel. The titanium dioxide was added as the oxide to the catalyst, whilst the molybdenum oxide was produced *in situ*.

The catalytic effectiveness in the catalytic oxidation of carbon monoxide and hydrocarbons (HC) was tested and the results thereof are set out in Table II.

TABLE II
Effect of MoO₃ on Catalyst Resistance to SO₂

Temperature °C	CO oxidation (%)			
	Rt°	200°	300°	400°
Sample P1 (without)	60	90	100	100
Sample P2 (without)	57	87	100	100
Sample P3 TiO ₂ /MoO ₃	82	95	100	100
Sample P4 TiO ₂ /MoO ₃	79	92	100	100

Test conditions: steady state
Space velocity: 60 000 h
Gas composition: 1% CO, 0,9% O₂, 700 ppm HC, 2% moisture,
15 ppm SO₂, balance N₂.

The detrimental effect of SO₂ on the catalyst in the absence of TiO₂/MoO₃ is most noticeable at lower temperatures.

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CLAIMS

1.

A catalyst for use in catalysing the oxidation of carbon monoxide and hydrocarbons comprising an oxide support having captured thereon a noble metal in catalytically effective form, characterised by the presence of an oxide of titanium, molybdenum or a mixture thereof.

2.

A catalyst according to claim 1 wherein the oxide of titanium or molybdenum or mixture thereof is present in an amount of up to about 15 percent by mass of the catalyst.

3.

A catalyst according to claim 1 wherein the oxide of titanium or molybdenum or mixture thereof is present in an amount of up to about 10 percent by mass of the catalyst.

4.

A catalyst according to any one of the preceding claims wherein the oxide is provided in finely particulate form.

5.

A catalyst according to any one of the preceding claims wherein the surface area of the oxide is of the order of 80 to 200m²/g.



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6.

A catalyst according to any one of the preceding claims wherein the oxide support comprises zirconium oxide, cerium oxide or a mixture thereof, present in the catalyst in an amount of at least 50 percent by mass of the catalyst.

7.

A catalyst according to any one of the preceding claims wherein the oxide support comprises a mixture of zirconium and cerium oxide, the cerium oxide constituting at least 50 percent by mass of the mixture.

8.

A catalyst according to any one of the preceding claims wherein the noble metal is selected from gold, platinum, palladium, rhodium and silver.

9.

A catalyst according to any one of the preceding claims which also contains a transition metal in oxide form.

10.

A catalyst according to claim 9 wherein the transition metal oxide has a spinel structure.

11.

A catalyst according to claim 9 or claim 10 wherein the transition metal oxide is selected from cobalt oxide and ferric oxide.



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12.

A catalyst according to any one of claims 1 to 7 wherein the noble metal is gold and there is also present a transition metal oxide having a spinel structure, the gold being complexed with the transition metal oxide.

13.

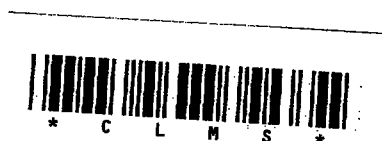
A catalyst according to claim 12 wherein the transition metal oxide is selected from cobalt oxide and ferric oxide.

14.

A method of oxidising carbon monoxide or a hydrocarbon in the presence of sulphur includes the step of catalysing the oxidation using a catalyst according to any one of the preceding claims.

15.

A method according to claim 14 wherein the sulphur is sulphur dioxide.



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PCT/US89/02375 discloses a catalytic composite comprising a first support which is a refractory inorganic oxide having dispersed thereon at least one noble metal component selected from the group consisting of platinum, palladium, rhodium, ruthenium and iridium and having dispersed thereon an overlayer comprising at least one oxygen storage component and a second support which is a refractory inorganic oxide.

GB-A-2006038 discloses a catalyst system comprising a support and a catalyst material including platinum and/or palladium carried on the support, characterised in that the support also carries molybdenum in an amount of at least ¼% by weight, based on the weight of the support, and not less than 7 times the weight of the platinum and/or palladium.

The ratio of noble metal to transition metal, when present, in the catalyst, can vary over a wide range. Generally, the atomic ratio of noble metal to the transition metal will not exceed 1:100.

The catalyst, when it contains both a noble metal and a transition metal oxide, may be made by the method described in PCT/GB 95/00136. The method involves impregnating the oxide support with a solution of the transition metal, optionally drying the product, exposing the impregnated product to a reducing atmosphere such as hydrogen or carbon monoxide at a temperature exceeding 300°C, impregnating the thus treated product with a solution of the noble metal and drying the impregnated product. The catalyst may be activated by exposing it to a temperature of at least 300°C, typically 300 to 700°C, in the presence of oxygen. The oxygen may be air or oxygen mixed with another gas.

The invention will now be illustrated by the following examples. In each case, the samples were prepared in duplicate containing the stated compositions. The comparative samples were prepared in a similar manner but without a stated component(s).

EXAMPLE 1

A catalyst was produced using the method generally disclosed in PCT/GB 95/00136 and comprised 0,5% gold, 9,5% cobalt, 80% zirconium oxide/cerium oxide and 10% titanium dioxide, all percentages being by mass. The cobalt was in the form of cobalt oxide having a spinel structure, and the gold was in association, i.e. complexed, with the cobalt oxide spinel. In producing the catalyst, the titanium dioxide was added as the oxide to the catalyst.



CLAIMS

1. A catalyst for use in catalysing the oxidation of carbon monoxide and hydrocarbons comprising an oxide support comprising zirconium oxide, cerium oxide or a mixture thereof, present in an amount of at least 50% by mass of the catalyst, having captured thereon gold and a transition metal oxide, the gold being complexed with the transition metal oxide, and an oxide of titanium, alone or as a mixture with molybdenum oxide, such oxide or mixture being present in an amount of up to 15% by mass of the catalyst.
2. A catalyst according to claim 1 wherein the oxide of titanium or mixture thereof with molybdenum oxide is present in an amount of up to about 10% by mass of the catalyst.
3. A catalyst according to any one of the preceding claims wherein the oxide support is provided in finely particulate form.
4. A catalyst according to any one of the preceding claims wherein the surface area of the oxide support is of the order of 80 to 200m²/g.
5. A catalyst according to any one of the preceding claims wherein the oxide support comprises a mixture of zirconium and cerium oxide, the cerium oxide constituting at least 50 % by mass of the mixture.
6. A catalyst according to any one of the preceding claims wherein the transition metal oxide has a spinel structure.
7. A catalyst according to any one of the preceding claims wherein the transition metal oxide is selected



from cobalt oxide and ferric oxide.

8. A method of oxidising carbon monoxide or a hydrocarbon in the presence of sulphur including the step of catalysing the oxidation using a catalyst according to any one of the preceding claims.

9. A method according to claim 8 wherein the sulphur is sulphur dioxide.

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