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OXIDATION CATALYST RESISTANT TO SULFATION

BACKGROUND OF THE INVENTION

The present invention relates to an oxidation catalyst which is resistant to sulfur oxides. In particular, the present invention is directed to an oxidation catalyst useful in purifying exhaust and waste gases and, more specifically, to an oxidation catalyst capable of converting carbon monoxide and hydrocarbons to carbon dioxide and water with high efficiency even in the presence of sulfur oxides.

The present invention also relates to a process for converting carbon monoxide and hydrocarbons such as contained in exhaust or waste gas streams to carbon dioxide and water even when the exhaust or waste gas streams contain sulfur oxide components. The invention is also directed to a process for converting sulfur dioxide to sulfur trioxide using the novel sulfur-resistant oxidation catalyst of the present invention.

Hydrocarbon and CO abatement in various waste and exhaust gas streams may be accomplished by reacting the waste or exhaust gas with air over a platinum-containing catalyst. Typically used at present is a catalyst similar to the auto exhaust catalyst which is comprised of platinum supported on alumina supports or alumina-containing supports which are often deposited over a ceramic honeycomb. Such catalysts are effective oxidation catalysts and deactivation of such catalysts are minimal when the waste or exhaust gas is devoid of sulfur oxides, to be referred to as SO_x, including SO_2. However, the exhaust and waste gases of many industrial operating systems including those cogenerating electricity and steam which are powered with diesel fuel or refining gas often contain up to a few hundred parts per million of

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SO_2. Under reaction conditions, SO_2 oxidizes to SO_3 which in turn reacts with alumina to form aluminum sulfate and, thus, renders the alumina-containing oxidation catalysts inactive.

It is known to use oxidation catalysts which contain catalytic metals on refractory oxide supports other than alumina. Thus, supports comprising silica, titania, zirconia and mixtures of these oxides are known and such supports including the binary and ternary mixtures of the above oxides are known to be resistant to SO_x. Unfortunately, it is also known that it is difficult to anchor a precious metal such as platinum on a silica support. The weak interaction between silica and precious metals results in severe precious metal sintering at very moderate conditions drastically reducing the surface area and, thus, activity of the precious metal catalyst. Moreover, although titania and zirconia interact with precious metals to significantly reduce sintering of the precious metal, the high initial surface area of both zirconia and titania (anatase) is drastically reduced after calcination at 500°C. The loss in surface area of zirconia and titania at typical reactive oxidation conditions is unfavorable inasmuch as the loss in surface area results again in the sintering of the precious metal and deactivation of the catalyst.

Accordingly, it is an object of the present invention to provide an effective carbon monoxide oxidation catalyst.

It is another object of the present invention to provide an effective carbon monoxide oxidation catalyst which is stabilized against deactivation at the elevated temperatures of reaction.

It is another object of the present invention to provide an effective carbon monoxide oxidation catalyst which is stabilized against deactivation by the presence of SO_x.

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It is a further object of the present invention to provide an effective oxidation catalyst which can effectively oxidize gaseous sulfur-containing compounds to SO_2, SO_3 or mixtures thereof.

Yet another object of the present invention is to utilize a sulfur-resistant carbon monoxide oxidation catalyst in a process for purifying waste and exhaust gas streams of hydrocarbons and carbon monoxide.

Yet still another object of the present invention is to provide a process for effectively oxidizing SO_2 to SO_3 in the presence of a stabilized oxidation catalyst.

SUMMARY OF THE INVENTION

In accordance with the present invention, an oxidation catalyst is provided which is resistant to deactivation by sulfur oxides and which is useful in the oxidation of carbon monoxide and hydrocarbons such as is present in waste and exhaust gas streams which further contain SO_x. The catalyst of this invention is also useful in oxidizing SO_2 to SO_3.

The catalyst of this invention comprises refractory silica particles which have been coated with titania, zirconia or mixtures thereof and upon which coated silica particles contain a Group VIII precious metal including but not limited to platinum, palladium and rhodium. The coated particulate catalyst is then coated on a ceramic honeycomb support as a washcoat for use. An important feature of the invention is the coating of titania or zirconia on the refractory silica particles. In accordance with this invention, the titania and zirconia coating is achieved by adding a titanium or zirconium salt to coat and/or impregnate the silica particles, and calcining in air to convert the metal salt to the respective oxide. The precious metal is subsequently added to the coated silica by known means. Alternatively, the precious metal can be applied to silica particles which have been coated with titania or zirconia precursors, i.e., precipitated Ti or Zr salts, that will be converted to the respective oxides during calcination

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after the precious metal is applied or during use of the catalyst. It has been found that the coating of titania or zirconia stabilizes the silica against sintering and provides a surface where precious metal sintering is minimized. Moreover, it has been found the silica stabilizes the titania or zirconia coating against sintering at elevated temperatures. The washcoat of coated silica particles on the honeycomb is advantageous inasmuch as the precious metal is dispersed throughout the thickness of washcoat layer.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph illustrating the 800°C heat-aged stability of silica, zirconia and mixtures thereof.

Figure 2 is a graph illustrating the two hour heat-aged stability of silica relative to mixtures of titania and silica.

Figure 3 is a graph illustrating the 2% platinum dispersion on the catalyst of this invention relative to the amount of zirconia added to the silica support.

Figure 4 is a graph comparing SO_2 oxidation using the catalysts of this invention relative to a catalyst comprising 2% Pt/SiO_2.

Figure 5 is a graph illustrating the effectiveness of the catalyst of this invention in oxidizing CO upon aging of the catalyst with SO_2 compared to the effectiveness of a standard commercial catalyst.

DETAILED DESCRIPTION OF THE INVENTION

The oxidation catalyst of the present invention finds its preferred use in oxidizing carbon monoxide and hydrocarbons contained in exhaust and waste gas streams for conversion to CO_2 and water and wherein the waste and exhaust gas streams contain sulfur oxide compounds (SO_x). The catalyst of this invention is particularly useful in purifying exhaust gas from cogeneration units. In the catalyst of this invention, the alumina refractory base typically used in commercially available oxidation catalysts is replaced with silica which is stabilized by the addition of titania or zirconia to yield a base which

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can effectively anchor the precious metal component and is resistant to SO_x degradation and deactivation. In view of the SO_x resistance of the catalyst of this invention, the catalyst can also be used to oxidize gaseous sulfur-containing compounds to SO_2, SO_3 or mixtures thereof which has particular importance in various commercial applications involving the formation of sulfur-containing compounds including sulfuric acid and in the formation of various surface active agents. Moreover, oxidation of SO_2 to SO_3 is valuable in cleaning exhaust and waste gas streams of sulfur as the SO_3 is substantially easier to remove than SO_2.

The silica substrate is in the form of a refractory particulate having a sufficient surface area to be catalytically active, e.g. > 10 m^2/g, and is stabilized by coating the refractory silica particulate with titanium or zirconium oxide or a mixture thereof. The starting materials for the zirconia and titania coating are preferably in the form of metal salts which are coated onto the particulate silica surface and which are then converted to the oxide by calcination in an O_2-containing gas such as air. Useful inorganic salts can include the chlorides, nitrates and sulfates of the respective metals. Organic acid salts such as the acetates, oxalates, etc. are also useful. Upon coating with the metal salt, the coated silica is calcined at a temperature typically above 500°C. Alternatively, the source for the zirconia and titania coating can be colloidal titania and zirconia. Further still, the silica particles can be slurried with a titanium or zirconium salt solution as described above and then treated to precipitate a titanium or zirconium oxide precursor salt onto the surface of the silica prior to the addition of the precious metal. The titanium and zirconium precursor salt can be converted to the oxide subsequent to the addition of the precious metal. In its broadest form, this further alternative method involves the addition of any titanium and zirconium compound which is a precursor

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for titania or zirconia and which corresponding oxide can be formed prior to precious metal addition, subsequent to precious metal addition and even during the use of the catalyst.

It is an important aspect of this invention that the titania and zirconia addition to the silica be in the form of coating and/or impregnated into the silica. Thus, methods of forming mixed gels or co-precipitates of zirconia and/or titania with silica are not believed to be sufficient to provide the improvements in catalyst stability which have been found using the catalyst as prepared by the coating processes as above described. Thus, methods of co-precipitating or co-gelling titania or zirconia with silica are not considered part of the present invention.

To provide the improved heat stability and resistance to SO_x which has been found in the catalyst of this invention, the titania and zirconia should comprise greater than 5 wt.% of the stabilized silica. Coating weights of 10 to 25 wt.% are preferred to sufficiently provide the necessary stabilization. Coating weights above 25% are not believed to provide any substantial increase in stability although coating weights above 25% can be used as no detriment in catalyst stability or effectiveness is believed to occur at the higher coating loadings. Coating weights of greater than 5 wt.% to 25 wt.% correspond to 0.17 mg/m^2 of BET surface area to 0.83 mg/m^2 of BET surface area.

Subsequent to the formation of the titania or zirconia coating or precursor thereof on the silica particulate, the stabilized silica is coated with the precious metal component. Useful precious metals for the oxidation catalyst of this invention include platinum, palladium, ruthenium, iridium, rhodium, or a mixture thereof. The precious metal component can be added to the stabilized silica by an impregnation method, a kneading method or the like conventionally used method. A method of impregnation is preferred. It is preferable to add the

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precious metal component on the stabilized silica in an amount of from about 0.1 to 3% by weight based on the weight of the catalyst. As starting materials for the precious metal component, there can be used salts and complexes of precious metals such as chloroplatinic acid, platinum-amine complexes, as well as the chlorides and nitrates of the various precious metals.

The catalyst of this invention containing the precious metal dispersed upon the titania- or zirconia-stabilized silica particulate itself is applied as a layer or multiple layers of coated silica particles on a carrier such as a refractory honeycomb carrier. Thus, the catalyst is dispersed within a liquid wash coat which then impregnates the honeycomb carrier by methods well known in the art. This supported catalyst is preferred as the precious metal is highly dispersed throughout the washcoat and is not merely applied as a surface coating that is more readily damaged and deactivated. Alternatively, although not preferred, it is possible to apply the zirconia stabilized silica as a wash coat on the honeycomb carrier and then subsequently impregnate the treated carrier with the precious metal component.

The coated particulate catalyst of this invention may also be molded such as by a tableting method, an extrusion method, a rolling granulated method and the like conventionally used method to form a catalyst having any desired shape such as cylinder, sheet, ribbing, corrugated sheet, donut, grid, etc. such instances, if desired, the catalyst of this invention can be supported on well known carriers such as alumina, silica, silica-alumina, bentonite, diatomaceous earth, silicon carbide, titania, zirconia, magnesia, pumice and active carbon.

The stability of the present oxidation catalyst with respect to both elevated temperature and contact with SO_x has been studied experimentally. While exact theories as to how the improvements in stability have occurred cannot be presented, empirical comparative results may be illuminating. Thus, it has been found that the addition

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of ZrO_2 or TiO_2 to silica has a pronounced positive effect on stabilizing the SiO_2 against sintering. Figure 1 shows that the addition of 5% ZrO_2 to a silica surface resulted in a highly heat stable support. Thus, the surface area of the ZrO_2/SiO_2 (%ZrO_2 = 5-25%) remained almost unchanged after calcination for several days at 800°C. Similar stabilization of silica was also found upon a TiO_2 addition as shown in Fig. 2. As further shown in Fig. 1, pure silica, on the other hand, lost more than 60% of its surface area after 24 hours at 800°C.

An important characteristic that differentiates the TiO_2- and ZrO_2- stabilized silica prepared by this invention vs binary titania- and zirconia-silica compounds is the stabilization of the ZrO_2 and TiO_2 phases by the silica in the catalysts of this invention. The precise nature of the interaction between ZrO_2 or TiO_2 and silica leading to stabilization is not clear, however, an interesting observation of the ZrO_2 and TiO_2 structure has been noted. X-ray diffraction (XRD) of ZrO_2/SiO_2 base as prepared by this invention shows that the zirconia produced on the silica surface yielded a diffraction pattern which matched tetragonal zirconia (beta zirconia). The beta phase is usually formed by calcining pure zirconia at temperatures of 1000°C or higher compared to monoclinic zirconia (baddeleyite) which is formed at lower temperatures. Stabilization of the zirconia by silica assures that the silica will remain covered with ZrO_2, thus, minimizing the interaction of the precious metal such as platinum with the silica base. In the catalyst of this invention, lower ZrO_2 loadings of 5 wt.% were believed to be crystalline even though no XRD pattern was observed. Typically, a diffraction pattern of zirconia will on be observed if the ZrO_2 crystallites are in excess of 40 A and, thus, smaller crystallites are beyond detection. Accordingly, is believed that the zirconia at the low 5 wt% level was highly dispersed with crystallites smaller than 40 A. Binary zirconia silica made by coprecipitation or cogellation have no XRD

pattern and have much of the surface consisting of exposed silica. Exposed silica acts as a poor support for precious metals resulting in severe catalyst deactivation by precious metal sintering.

Similar observations have been found for titania-stabilized silica formed in accordance with the present invention. Titania (TiO_2) in the anatase phase is stable at temperatures less than 500°C. Surprisingly, it has been found that TiO_2 supported on SiO_2 was present in the anatase phase even after calcination in air at 900°C for several hours. The average titania crystallite size, measured by XRD, remained less than 40 A after calcination at 500°C. This clearly indicates that the titania, in the anatase phase, is highly dispersed and stabilized by the silica. It is interesting to note that the anatase titania is the least stable titania phase. On the contrary, a binary titania-silica prepared from a cogel, with similar chemical composition, was completely amorphous with no titania XRD pattern.

The function of highly dispersed zirconia or titania coating on the silica is to anchor the precious metal. This minimizes precious metal sintering and, thus, allows the catalyst to retain high activity at reaction conditions. Silica is a neutral support for precious metals deposition. The weak interaction between SiO_2 and precious metal results in severe precious metal sintering at very moderate conditions. On the contrary, TiO_2 and ZrO_2 interact with precious metals to significantly reduce precious metal sintering. A major problem, however, in using zirconia or titania as a sole support for precious metals is the loss in support surface area at reaction conditions. Both zirconia and titania (Anatase) have a high initial surface area (100-150 m^2/g), but surface area decreases significantly after calcination at 500°C. The loss in surface area of zirconia or titania at reaction conditions, is unfavorable since such loss results in precious metal sintering.

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Therefore, covering the silica particulate with stable metal oxides such as ZrO_2 or TiO_2, using the preparation procedure as described above with respect to the present invention is very favorable relative to reducing precious metal sintering. Covering the silica surface with ZrO_2 or TiO_2 is therefore essential for higher precious metal dispersion and superior catalytic performance. The extent of the silica surface covered depends primarily on the preparation procedure as well as on the amount of Tio_2 or ZrO_2 used. From CO chemisorption experiments, a measure of Pt dispersion, on a 2% $Pt/ZrO_2/SiO_2$ with varying amounts of ZrO_2, it was concluded that the Pt dispersion increased significantly as the ZrO_2 level was increased from 5 to 10% by weight (Fig. 3). An increase in Pt dispersion was observed, but to a lesser extent, as the ZrO_2 level was increased between 10 and 25%. At the 25% level of ZrO_2, the silica surface was covered with zirconia, consequently, the Pt would have substantially been in contact with zirconia and not silica. This resulted in effective dispersion of the Pt after calcination at 500°C for several hours. On the contrary, a binary support would have most of the silica exposed which would result in much Pt being anchored to silica. Pt anchored to a silica support always leads to sintering and loss in metal dispersion even at temperatures as low as 350-400°C. This is a considerably lower temperature than required to carry out many chemical reactions. Pt anchored on a zirconia-stabilized silica support, as per this invention, retains small Pt crystallites even after calcination in air at 700°C.

Similar results were also observed for the titania-stabilized silica catalyst (2% $Pt/TiO_2/SiO_2$) with TiO_2 level at 15 and 30%. XRD pattern showed that the TiO_2 remained in the anatase phase with crystallites less than 60 A even after calcination at 700°C which indicates that TiO_2 remained highly dispersed. The Pt crystallites on the 30% TiO_2/SiO_2 support, after calcination at 500°C, were

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smaller than the detectability limit of the XRD, indicating high dispersion, see Table 1. The Pt crystallites on the 15% TiO_2/SiO_2 support, calcined to similar conditions (500°C), were measured at 50 A which is still considerably well dispersed. Similar results were observed from CO chemisorption measurements as indicated in Table 1. Table 1 shows higher Pt dispersion with increase in TiO_2 (0-30%) coverage of the SiO_2 surface. The results clearly indicate that higher coverage of the silica surface with TiO_2 or ZrO_2 is more favorable for better precious metal dispersion.

TABLE 1

Catalyst	Calc.T	CO Uptake (cc/g)	Pt Cryst. (XRD, A)	TiO_2 Cryst. (XRD A)
A	500	.07	150	NA
B	500	.41	53	*
C	500	.94	*	30

Catalyst A = 2% Pt/SiO_2
Catalyst B = 2% Pt/15% TiO_2/SiO_2
Catalyst C = 2% Pt/30% TiO_2/SiO_2

CO Uptake is a measure of exposed Pt surface. Higher numbers indicate higher dispersion.

NA = Not applicable and
* = Below detection limits

The higher Pt dispersion on the zirconia- and titania-stabilized silica, prepared according to the present invention, also resulted in higher SO_2 conversion in the SO_2 oxidation reaction. Conversion of SO_2 over 2 wt.% Pt/SiO_2 catalyst was initially very low and the catalyst activity became nil in a short time on stream. On the other hand, SO_2 conversion activity was considerably increased using a 2 wt.% Pt catalyst (Fig. 4) due to addition of 25 wt.% ZrO_2 or 25 wt.% TiO_2 to the SiO_2 surface.

The following examples further illustrate the preparation and use of the catalyst of this invention. The Examples are to be construed as illustrative only and

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not for the purpose of limiting the scope of the invention to only the embodiments shown therein.

EXAMPLE 1

Preparation of $Pt/TiO_2/SiO_2$A catalyst was prepared by adding 635 g of Tyzor LA (A titania compound from Dupont containing 14.2% TiO_2) to 410 g of silica particles (SYLOID 74 from Davison), mixing well for 1 hour followed by drying and calcination at 700°C. 54.3 g of Pt amine salt was diluted with water to make approximately 8 g of Pt solution. The TiO_2/SiO_2 was mixed with the Pt solution and the Pt fixed on the catalyst by addition of an acetic acid solution. Water was then added to make a 30% solid slurry and the slurry applied onto a honeycomb to give a final product of 38 g of Pt/cu. ft. The catalyst was dried and calcined at 500°C. This catalyst was identified as Catalyst A.

EXAMPLE 2

Preparation of $Pt/CeO_2/Al_2O_3$

CeO_2/Al_2O_3 was prepared by incipient wetness impregnation of a cerium nitrate solution onto Al_2O_3. The support was then dried and calcined at 700°C for 2 hours. The preparation and deposition of the $Pt/CeO_2/Al_2O_3$ catalyst was similar to Example 1 and identified as Catalyst B. Catalyst B had a composition similar to Catalyst A given as 38 g of Pt/Ft^3. of the honeycomb.

EXAMPLE 3

Catalysts A and B were tested fresh (virgin) for CO oxidation at several temperatures. The CO concentration was 250 ppm with a Gas Hourly Space Velocity of 600,000 hr^{-1}. The results of the test are given in Table 2.

TABLE 2

	CO ppm	SO_2 ppm	Light Off T(°C)	% CO Conv @ (°C) 100	150	200	250
Cat A	250	0	120	45	58	65	70
Cat B	250	0	120	40	55	65	70

Light off temperature was measured as the minimum temperature required to give 50% CO conversion.

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Table 2 clearly indicates that both catalysts tested fresh had similar activity. No difference in performance could be deduced when the catalysts were tested fresh in the absence of SO_2.

EXAMPLE 4

Catalysts A and B were tested for CO oxidation in the presence of 200 ppm of SO_2. This experiment mimicked cogeneration unit operation. The CO light off temperature as well as the CO conversion at several reaction temperatures is given in Table 3.

TABLE 3

Catalyst	GHSV	CO ppm	SO_2 ppm	Light Off T (°C)	% CO Conversion @ Temp. (°C) 100	150	200	250
A	500,000	250	200	250	0	15	47	50
B	500,000	250	200	>260	0	7	25	45

The non-alumina based support had lower light off temperature as well as higher CO conversion at all temperatures tested. This clearly indicates that in the presence of SO_2, the catalyst per this invention is more active than catalyst B in converting CO and is less susceptible to sulfation. Alumina based catalyst sulfates (forms aluminum sulfates) which results in catalyst deactivation.

EXAMPLE 5

Catalysts A and B were aged in SO_2 /steam at 950°F for 16 hours to determine the effect of sulfation on their performance. The catalysts were aged for 16 hours in 2% SO_2, 88% air, and 10% steam. The catalysts were then tested for CO oxidation in the absence of SO_2. The results in Table 4 clearly indicate that the TiO_2/SiO_2 based catalysts have higher tolerance for the SO_2/steam compared to the alumina supported catalyst.

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TABLE 4

Catalyst	CO ppm	Light Off T (°C)	% CO Conversion @ Temp. (°C) 100	150	200	250	300
A	250	140	45	52	55	57	60
B	250	200	10	30	50	57	62

The CO conversion of the non-alumina based catalyst ($Pt/TiO_2/SiO_2$) resembled that of fresh catalyst. The poisoning effect of the SO_2/SO_3 on the alumina based catalyst seemed to be permanent. On the contrary, the $Pt/TiO_2/SiO_2$ recovered most of its activity after aging in the SO_2/air/steam atmosphere. This may be related to the acidic properties of the support that interacts weakly with the SO_3 formed during aging. On the other hand, alumina would sulfate and, thus, result in catalyst deactivation.

EXAMPLE 6

This was similar to Example 5 except that during testing SO_2 (200 ppm) were introduced with the CO feed. Results are given in Table 5.

TABLE 5

Catalyst	CO ppm	SO_2 ppm	Light Off T	% CO Conversion @ (Temp°C) 125	150	200	250
A	250	200	250	8	15	42	50
B	250	200	270	0	8	25	45

EXAMPLE 7

This example illustrates the synthesis procedure for 2% Pt/25% ZrO_2/SiO_2.

330 g of zirconyl nitrate was dissolved in 480 ml of hot water. 400 g of SiO_2 particles (SYLOID 74 from Davison) were mixed with the zirconyl nitrate solution for at least one hour to impregnate the silica. The mixture was dried at 120°C for 16 hours and calcined at 880°C.

392 g of the 25% ZrO_2/SiO_2 support was mixed with 400 ml of Pt amine salt solution containing 8 g Pt (made by

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diluting 54.3 g of Pt amine salt (% Pt = 14.73) solution with 400 ml of water). 40 ml of acetic acid were added during mixing for 2 hours. A slurry of this catalyst was prepared by mixing the wet cake catalyst above with 400 ml of water (solid content = 33%). The slurry was ball milled for 19 hours and then applied to 200 cells/in_2 honeycomb (6x6x3 inches honeycomb) so that the finished coated honeycomb had a Pt pick-up of 41 g of Pt per ft_3. Fig. 5 shows the CO conversion of the above catalyst after exposure to SO_x. The standard commercial catalyst used was catalyst B above. As can be seen, the catalyst of this invention had a substantially higher activity than the alumina-containing catalyst.

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CLAIMS:

1. A sulfur-resistant oxidation catalyst comprising silica, a coating of titania or zirconia or a mixture thereof or precursors of said oxides on said silica and at least one precious metal supported on said coated silica.

2. The catalyst of claim 1 wherein said titania or zirconia coating is present in amounts of from at least 5 wt.% based on said coated silica.

3. The catalyst of claim 1 wherein said titania or zirconia coating is present in amounts of at least about 10 wt.% based on said coated silica.

4. The catalyst of claim 3 wherein said titania or zirconia coating is present in amounts of at least about 10 to about 25 wt.% based on said coated silica.

5. The catalyst of claims 1, 2 or 3 wherein said silica is in the form of a silica particle.

6. The catalyst of claim 5 wherein said titania or zirconia coating is applied as a titanium or zirconium salt which is calcined in an oxygen-containing gas to form the respective metal oxide.

7. The catalyst of claims 1, 2 or 3 wherein said titania or zirconia coating is applied as a titanium or zirconium salt which is calcined in an oxygen-containing gas to form the respective metal oxide.

8. The catalyst of claims 1 or 6 or wherein said precious metal is platinum.

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9. A sulfur-resistant oxidation catalyst comprising a ceramic honeycomb coated with a catalytic washcoat containing particles of silica coated with titania or zirconia or a mixture thereof or a precursor of said oxides and at least one precious metal supported on said coated silica particles.

10. The catalyst of claim 9 wherein said titania or zirconia coating is present in amounts of from at least 5 wt.% based on said coated silica.

11. The catalyst of claim 9 wherein said titania or zirconia coating is present in amounts of at least about 10 wt.% based on said coated silica.

12. The catalyst of claim 11 wherein said titania or zirconia coating is present in amounts of at least about 10 to about 25 wt.% based on said coated silica.

13. The catalyst of claims 9, 10 or 11 wherein said titania and zirconia coating is applied as a titanium or zirconium salt which is calcined in an O_2-containing gas to form the respective metal oxide.

14. The catalyst of claim 13 wherein said precious metal is platinum.

15. A process for purifying waste and exhaust gas steams of carbon monoxide and/or hydrocarbons wherein said exhaust and waste gas stream also contains SO_x components, comprising contacting said waste and exhaust stream with an 02-containing gas at a temperature sufficient to cause oxidation of said carbon monoxide and hydrocarbons and in the presence of a sulfur-resistant oxidation catalyst, said oxidation catalyst comprising silica coated with titania or zirconia or a mixture thereof or precursors of said oxides and at least one precious metal supported on said coated silica.

16. The process of claim 15 wherein said titania or zirconia coating is present in amounts of from at least 5 wt.% based on said coated silica.

17. The process of claim 15 wherein said titania or zirconia coating is present in amounts of at least about 10 wt.% based on said coated silica.

18. The process of claim 17 wherein said titania or zirconia coating is present in amounts of at least about 10 to about 25 wt.% based on said coated silica.

19. The process of claims 15, 16 or 17 wherein said silica is in the form of a silica particle.

20. The process of claim 19 wherein said titania and zirconia coating is applied as a titanium or zirconium salt which is calcined in an O_2-containing gas to form the respective metal oxide.

21. The process of claims 15, 16 or 17 wherein said titania and zirconia coating is applied as a titanium or zirconium salt which is calcined in an O_2-containing gas to form the respective metal oxide.

22. The process of claims 15 or 20 wherein said precious metal is platinum.

23. A process for purifying waste and exhaust gas steams of carbon monoxide and/or hydrocarbon wherein said exhaust and waste gas stream also contains SO_x components, comprising contacting said waste and exhaust stream with an O_2-containing gas at a temperature sufficient to cause oxidation of said carbon monoxide and hydrocarbon and in the presence of a sulfur resistant oxidation catalyst, said oxidation catalyst comprising a ceramic honeycomb coated with a catalytic washcoat containing particles of silica coated with titania or zirconia or a mixture thereof or precursors of said oxides and at least one precious metal supported on said coated silica particles.

24. The process of claim 23 wherein said titania or zirconia coating is present in amounts of from at least 5 wt.% based on said coated silica.

25. The process of claim 23 wherein said titania or zirconia coating is present in amounts of at least about 10 wt. based on said coated silica.

26. The process of claim 25 wherein said titania or zirconia coating is present in amounts of at least about 10 to about 25 wt.% based on said coated silica.

27. The process of claims 23, 24 and 25 wherein said titania and zirconia coating is applied as a titanium or zirconium salt which is calcined in an O_2-containing gas to form the respective metal oxides.

28. The process of claims 23 and 27 wherein said precious metal is platinum.

29. A process for oxidizing gaseous sulfur-containing compounds to SO_2, SO_3 or mixtures thereof comprising contacting said gaseous sulfur-containing compounds in an O_2-containing gas at a temperature sufficient to oxidize said sulfur-containing compounds and in the presence of a sulfur-resistant oxidation catalyst, said catalyst comprising silica, a coating of titania or zirconia or a mixture thereof or precursors of said oxides and at least one precious metal supported on said coated silica.

30. The process of claim 29 wherein said titania or zirconia coating is present in amounts of from at least 5 wt.% based on said coated silica.

31. The process of claim 29 wherein said titania or zirconia coating is present in amounts of at least about 10 wt. based on said coated silica.

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32. The process of claim 31 wherein said titania or zirconia coating is present in amounts of at least about 10 to about 25 wt.% based on said coated silica.

33. The process of claims 29, 30 or 31 wherein said silica is in the form of a silica particle.

34. The process of claim 33 wherein said titania and zirconia coating is applied as a titanium or zirconium salt which is calcined in an O_2-containing gas to form the respective metal oxide.

35. The process of claims 29, 30 or 31 wherein said titania and zirconia coating is applied as a titanium or zirconium salt which is calcined in an O_2-containing gas to form the respective metal oxide.

36. The process of claims 29 or 34 wherein said precious metal is platinum.

37. A process for oxidizing SO_2 to SO_3 comprising contacting said SO_2 in an O_2-containing gas at a temperature sufficient to oxidize said SO_2 and in the presence of a sulfur resistant oxidation catalyst, said catalyst comprising a ceramic honeycomb coated with a catalytic washcoat containing particles of silica coated with titania or zirconia or a mixture thereof or precursors of said oxides and at least one precious metal supported on said coated silica particles.

38. The process of claim 37 wherein said titania or zirconia coating is present in amounts of from at least 5 wt.% based on said coated silica.

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39. The process of claim 37 wherein said titania or zirconia coating is present in amounts of at least about 10 wt.% based on said coated silica.

40. The process of claim 39 wherein said titania or zirconia coating is present in amounts of at least about 10 to about 25 wt.% based on said coated silica.

41. The process of claims 37, 38 or 39 wherein said titania and zirconia coating is applied as a titanium or zirconium salt which is calcined in an O_2-containing gas to form the respective metal oxides.

42. The process of claim 41 wherein said precious metal is platinum.

43. The process of claim 37 wherein said SO_2 is present in an exhaust or waste gas stream which is contacted with said ceramic honeycomb.

* C L M S *

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