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(54) Title: OXIDATION CATALYST AND METHOD FOR DESTRUCTION OF CO, VOC AND HALOGENATED VOC

(57) **Abstract**: An oxidation catalyst deposited on a substrate is described for the destruction of CO and volatile organic compounds, in particular halogenated organic compounds, from an emissions stream at temperatures from 250°C to 450°C. The oxidation catalyst includes at least two platinum group metals, one of which is either platinum or ruthenium, supported on refractory oxides, such as a solid solution of CeO_2 and ZrO_2, and tin oxide and/or silica.

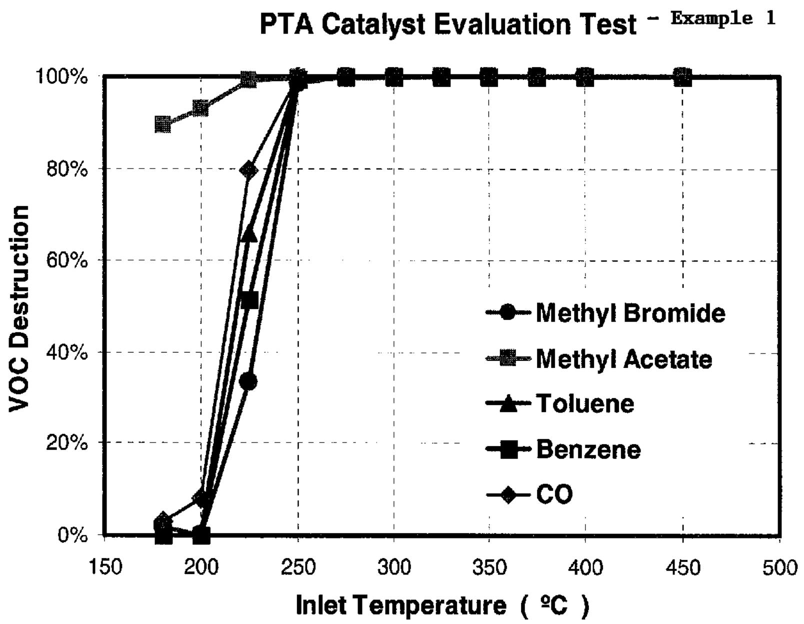

FIGURE 1

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OXIDATION CATALYST AND METHOD FOR DESTRUCTION OF CO, VOC AND HALOGENATED VOC

TECHNICAL FIELD

This disclosure relates to oxidation catalysts deposited on a substrate for the destruction of CO and volatile organic compounds (VOC), particularly halogenated organic compounds, from gaseous emissions streams in plants, particularly chemical plants, and processes for their use. In particular, oxidation catalysts deposited on a substrate are described, wherein the oxidation catalyst includes at least two platinum group metals, such as ruthenium and platinum, supported on a refractory oxide, comprising a solid solution of CeO_2 and ZrO_2, and either or both of tin oxide and silica. The catalysts that include the platinum group metals supported on a refractory oxide may be stabilized by addition of one or more rare earth metal oxides.

BACKGROUND ART

The treatment of gaseous emissions containing volatile organic compounds has been an increasing concern in recent years. Chemical plant off-gas emissions containing volatile organic compounds, particularly halogenated volatile organic compounds, are highly toxic pollutants for the environment and may be dangerous to human beings. Several technologies have been developed for the removal of such chemical plant off-gas emissions including thermal incineration, adsorption, and catalytic oxidation.

Thermal incineration requires high operating temperatures and high capital cost facilities. If the gaseous stream also includes halogenated compounds, thermal incineration can create toxic halogenated compounds under some conventional operating conditions. Thus, thermal incineration may not be effective.

In some circumstances, adsorption by adsorbents, such as carbon, is an alternative process for the removal of such volatile organic compounds from off-gas emissions. However, this process does not destroy the pollutants but merely concentrates them. Furthermore, adsorption efficiency can be adversely impacted by fluctuating concentrations of the volatile organic compounds that may be present in the off-gas emissions.

Alternatively, catalytic oxidation is an energy efficient and economical way of destroying off-gas emissions, such as carbon monoxide and volatile organic compound emissions. Oxidation catalysts, such as precious metal catalysts and base metal catalysts, have previously been used for the destruction of volatile organic compounds and carbon monoxide in chemical plants. However, when the volatile organic compounds to be removed contain halogenated organic compounds, traditional oxidation catalysts cannot be used because they are quickly poisoned by these halogenated organic compounds.

As an example of a current problem in the removal of halogenated organic compounds, off-gas emissions from purified terephthalic acid (PTA) or purified isophthalic acid (PIA) production plants normally contain carbon monoxide, methyl bromide, and various VOCs. Before these off-gases can be vented to the atmosphere, these compounds must be destroyed, normally by catalytic oxidation. Current catalysts used for such oxidation process are required to operate at high temperatures to minimize or eliminate the formation of polybromobenzenes, which are solid and can cause plugging or blockage of process pipe lines.

The catalytic process for the removal of VOCs can occur at high pressure, such as high pressure catalytic oxidation, or at low pressure, such as recuperative catalytic oxidation and regenerative catalytic oxidation. With a regenerative catalytic oxidation, process gas with VOC contaminates enters the regenerative catalytic oxidation through an inlet stream which is preheated. The process gas with the contaminates is progressively heated as it moves through the ceramic heat exchange media designed into the regenerative system. Compared to a Regenerative Thermal Oxidizer (RTO), an RCO, destroys contaminates at a much lower temperature (typically 50% lower) than conventional RTOs, which reduces the quantity of fuel that is required to operate the pollution control equipment. In addition, as the VOCs are oxidized across the catalyst, they release energy and reduce the need for auxiliary fuel. Depending upon the quantity of VOCs contaminates that are present, energy released from their combustion can result in an operation which is self-sustaining or close to self-sustaining. The regenerative catalytic oxidizers/process also operate at linear flow rates that are significantly lower then conventional recuperative catalytic oxidizers/processes for the reduction of VOCs. Thus, regenerative catalytic oxidizers/processes require catalysts which are designed to match the low linear velocities, and occupy a larger volume of total area, and operate at lower temperatures with lower pressure drop. By use of the regenerative catalytic oxidizers, the costs of air pollution control system can be significantly reduced.

Although prior art systems have been useful for the treatment of some types of emissions, there is still a need to develop improved catalysts for the destruction of CO and volatile organic hydrocarbons, particularly halogenated VOCs for use with various types of gaseous emission streams and with various air pollution control systems, such as regenerative catalytic oxidizers.

The present disclosure provides solutions to the aforesaid problems by offering more active catalytic compositions which oxidize VOCs, particularly halogenated organic compounds, at temperatures lower than are used for conventional oxidation catalysts and which exhibit lower pressure drop, and processes for their production and use.

DISCLOSURE OF EMBODIMENTS OF THE INVENTION

One embodiment of the invention are oxidation catalysts deposited on a substrate for the destruction of CO and VOCs, particularly halogenated VOCs, from an emissions stream, wherein the oxidation catalyst comprises at least two platinum group metals, one of which preferably consists of ruthenium, with platinum as an alternative preferred platinum group metal, supported on refractory oxides comprising high surface area materials, including preferably a solid solution of CeO_2 and ZrO_2; and silica and/or tin oxide. In one embodiment, the oxidation catalyst is utilized for the destruction of off-gas emissions at temperatures from 250 - 450°C while exhibiting lower pressure drop, when using lower cell density monoliths (for example - 100 cpsi substrates exhibit more than three times lower pressure drop than 400 cpsi substrates used in conventional catalytic systems). The refractory oxides may be stabilized by blending with one or more rare earth metal oxides. The substrate may be a honeycomb structure, a monolithic structure or spherical beads.

Another embodiment of the invention are processes for the preparation of oxidation catalysts supported on a substrate for the destruction of CO and VOCs, particularly halogenated volatile organic compounds, from an emissions stream operating at temperatures from 250 - 450°C. The processes may comprise preparing and blending an aqueous mixture slurry of high surface area refractory oxides, such as a solid solution of CeO_2 and ZrO_2 with silica and/or tin oxide; coating the substrate with the blended aqueous mixture slurry; drying and calcining the coated substrate; depositing at least two platinum group metal precursor materials on the calcined coated substrate, such as ruthenium and platinum or ruthenium or platinum and an additional platinum group metal, and calcining the platinum group metal coated substrate. Alternatively, the platinum group metals can be blended with the other components and deposited on the substrate in a single processing step. In one embodiment, the refractory metal oxides are stabilized by the addition of one or more rare earth metal oxides that are added to the aqueous mixture.

Yet another embodiment of the invention are processes for the destruction of CO and VOCs, particularly halogenated VOCs, from off-gas emissions, particularly chemical plant off-gas emissions including high pressure catalytic oxidation, recuperative catalytic oxidation and regenerative catalytic oxidation, comprising passing said emissions over the above-described catalyst at temperatures from 250°C - 450°C.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing the destruction of CO and various VOCs, including a halogenated VOC over the catalyst of Example 1.

Figure 2 is a graph showing the destruction of CO and various VOCs, including a halogenated VOC over the catalyst of Example 2.

Figure 3 is a graph showing the destruction of various organic compounds including a halogenated VOC over the catalyst of comparative Example 3.

Figure 4 is a graph showing the destruction of various organic compounds including a halogenated VOC over the catalyst of comparative Example 4.

Figure 5 is a graph showing the XRD of a solid solution of La-doped ceria-zirconia with single phase ceria cubic structure, which is used in Example 1.

Figure 6 is a graph showing the destruction of CO and various VOCs including a halogenated VOC over the catalyst of Example 5 at space velocity 9600 /hr.

MODES FOR CARRYING OUT EMBODIMENTS OF THE INVENTION

Embodiments of the invention relate to oxidation catalysts, particularly useful for destruction of off-gas emissions, particularly VOCs, including halogenated VOCs. In particular, one embodiment of the invention relates to an oxidation catalyst deposited upon a substrate to oxidize CO and VOCs, particularly halogenated VOCs, from off-gas emissions streams operating at temperatures from 250°C - 450°C, which exhibit low pressure drop. The oxidation catalyst, after deposition on a substrate, can be placed in a catalytic reactor device for the off-gas destruction, such as high pressure catalytic oxidation, recuperative catalytic oxidation and regenerative catalytic oxidation.

The device for destroying CO and VOCs, particularly halogenated VOCs, from an emissions stream, particularly a chemical plant off-gas emission stream, is comprised of a substrate, which has deposited thereon a catalytic material, such as an oxidation catalyst. The substrate can be selected from conventional monolith substrates, ceramic saddle supports and spherical beads supports, utilizing a honeycomb, monolith, or bulk packing structure through which the emissions pass. The substrate may have significant flow-through capacity so as not to prevent or restrict significantly the flow of emissions through the substrate thereby exhibiting lower pressure drop.

The catalytic material has shown use with conventional high cell density substrates, such as 200 to 400 cpsi (30-60 cells per square centimeter) and has shown particular use with low cell density substrates, such as 50 to 100 cpsi (100 cpsi = 15.5 cell per square centimeter).

The substrate may be produced from ceramic materials, such as alumina, silica, titania, zirconia, magnesia, silica-alumina, silica-zirconia, titania-zirconia, titania-silica, alumina-titania, alumina-zirconia, silicon carbide, ceramic cordierite, mullite and mixtures or combinations thereof. Alternatively, metallic or metallic alloy substrates, such as those produced from stainless steel, iron-chromium alloys, nickel-chromium-iron alloys with or with aluminum, and other such metallic substrates may be used. In one embodiment, the substrates are formed from commercially available cordierite, mullite, silicon carbide, iron-chromium alloys and stainless steel materials.

The substrate may be coated with the inventive oxidation catalyst. The oxidation catalyst are formed from at least two platinum group metals, one of which consists of ruthenium or platinum, supported on one or more high surface area refractory oxides. In one embodiment, the platinum group metals include ruthenium, supported on a solid solution of CeO_2 and ZrO_2, and silica and/or tin oxide. In another embodiment, the refractory oxides are stabilized with one or more rare earth metal oxides.

The platinum group metals are selected from the group consisting of ruthenium, platinum, palladium, rhodium, rhenium and osmium. In one embodiment, the preferred platinum group metals are ruthenium or platinum, preferably ruthenium, and at least one additional platinum group metal, preferably a combination of ruthenium and platinum. In another embodiment, only ruthenium and platinum are present. The choice of the platinum group metals may be influenced by the type of compounds present in the off-gas emissions. For example, it has surprisingly been discovered that ruthenium compounds are more active for the destruction of halogenated VOCs, such as methyl bromide, while platinum compounds are more active for the destruction of aromatic VOCs, such as benzene or toluene. Catalysts that contain only ruthenium and platinum perform better than catalysts which contain only one of the precious metals group. When ruthenium and platinum are used as the platinum group metals, the ratio of the ruthenium to the platinum metal deposited upon the catalyst may be from 20:1 to 1:20, by weight, and alternatively from 5:1 to 1:1, by weight. The combination of platinum and ruthenium only without other platinum group metals in the suggested ratios also performs better than combinations of two or more other precious metals, including combinations of ruthenium with a precious metal other than platinum or combinations of platinum with a precious metal other than ruthenium.

The platinum group metal precursor materials, which are supported on the one or more refractory oxides, may be selected from the group consisting of ammonium hexachlororuthenate, bis(cyclopentadienyl)ruthenium, hexaammonineruthenium chloride, ruthenium chloride, ruthenium nitrosychloride, ruthenium nitrosylnitrate, ruthenium acetate, rutheniumoxide-hydrate, ruthenium acetylacetonate, tetrapropylammonium ruthenate, hexaammine ruthenium chloride, ruthenium oxide, platinum nitrate, platinum sulfite acid, ammonium platinum sulfite, dihydrogen hexahydroxyplatinate, hydrogen tetranitroplatinate, ammonium hexachloro platinate, dihydrogen hexahydroxy platinate, platinum acetylacetonate, platinum chloride, bis(ethanalammonium)-hexahydroxoplatinate, tetraammineplatinum nitrite, tetraammineplatinum nitrate, tetraammineplatinum hydroxide, platinum oxalate and other similar compounds and mixtures thereof.

The platinum group metal components may be supported on one or more high surface area refractory oxides. Generally, the surface area of the refractory oxides may be more than 50 m^2/g, and alternatively, greater than 100 to 800 m^2/g. The surface area referred to may be determined by a nitrogen physisorption method.

The refractory oxides chosen as the support may include at least cerium oxide and zirconium oxide, formed as a solid solution, with the ceria cubic structure crystal phase retained. For purposes of this disclosure, a "solid solution" consists of a uniform mixture of substances in solid form. Solid solutions often consist of two or more types of atoms or molecules that share a crystal lattice. In a one embodiment the zirconium oxide molecules share the cubic crystal structure with the ceria and the monoclinic or tetragonal crystal structure commonly associated with zirconia is generally not retained. The refractory oxides may also include other oxides of one or more compounds of Groups IIIB, III and IV, including alumina, silica, titania, zirconia, silica-alumina, alumina-zirconia, alumina-titania, silica-titania, silica-zirconia, and titania-zirconia.

However, in one embodiment, the preferred refractory oxides are ceria and zirconia, more preferably a solid solution of ceria-zirconia. When a solid solution of CeO_2 and ZrO_2 is used, the ZrO_2 comprises from 1 - 50 wt% of the solid solution. In alternative embodiments, the preferred refractory oxides are 10-30 wt% of ZrO_2 with 90-70 wt% of CeO_2, or 15-25 wt% of ZrO_2 with 85 wt%-75 wt% of CeO_2, both of which may or may not be present in a solid solution.

To enhance the stability of the refractory oxides to receive the platinum group metals, the refractory oxides may be stabilized by treatment with at least one rare earth oxide selected from lanthanum oxide, praseodymium oxide, neodymium oxide, gadolinium oxide, and yttrium oxide. In one embodiment, a combination of lanthanum oxide and praseodymium oxide is present. The quantity of the rare earth oxides comprises 1 to 5 wt% of the total of the combination of the refractory oxides and the rare earth oxides only.

An additional component of the oxidation catalyst may be silica and/or tin oxide. Silica may be used as an alternative to tin oxide depending on the composition of the emissions stream. Thus, in some circumstances, silica is preferable to tin oxide. Alternatively, depending on the emissions stream, the oxidation catalyst may contain tin oxide without silica or in combination with silica.

The silica may be a precipitated silica powder which has an amorphous phase with a surface area more than 200 m^2/g, a larger pore size diameter greater than 100 angstrom, and a particle size from 0.5 to 12 microns. Other types of amorphous silica, such as mesoporous molecular sieves MCM-41 and SBA-15, can be also used. These molecular sieves MCM-41 and SBA-15 also have a larger surface area, being greater than $200m^2/g$, larger pore volumes and uniform pore-size distributions of more than 100 angstrom, thereby allowing for higher dispersions of active components and better control on the particle size, as compared with conventional amorphous silica. Fumed silica, that may have larger surface area, is less desirable as a catalyst support due to its low porosity. Silica used as a support is especially useful for enhancing the activity of catalytic oxidation of CO and various VOC hydrocarbons, especially for oxidation of aromatic compounds. Silica has significantly lower surface acidity that leads to very weak capability to adsorb halogenated compounds, especially HBr/Br_2 for PTA plant off-gas destruction, which may result in poisoned catalysts. By using silica, the quantity of platinum group metals can be decreased while still achieving the same level of oxidation activity.

Tin oxide may be included as an additional, or alternative, component of the oxidation catalyst that is deposited upon the substrate. The tin oxide may be used as an alternative or in addition to silica. Tin oxide is especially useful for the oxidation of CO and various specific hydrocarbon materials. Tin oxide has significant oxygen storage capacity and can generate active oxygen for the oxidation of the hydrocarbon compounds. By using tin oxide, the quantity of platinum group metals can be decreased while still achieving the same level of oxidation activity. If tin oxide is added, it can be added in the form of particles with a size from 1 micrometer to 20 micrometers. Usually, commercial tin oxide products have low surface area. Notwithstanding, it is believed to enhance the catalyst performance for destruction of CO and aromatic VOC. Large surface area tin oxide, which may be stabilized by silica, greatly enhances catalyst performance. In one embodiment, it is preferred that tin oxide has a surface area from $2m^2/g$ to $200m^2/g$.

In an alternative embodiment, a combination of silica and tin oxide may be used, depending on the composition of the off-gas.

The oxidation catalyst of the invention may contain at least two platinum group metal compounds supported on the refractory oxide that may include a solid solution of CeO_2 and ZrO_2, with silica and/or tin oxide. In one embodiment, the concentration of the platinum group metal precursors, by weight, should be sufficient to obtain a metal loading of from 10 - 200 g/cf (0.35 g/l to 7.0 g/l), preferably from 50 - 100 g/cf (1.7 g/l to 3.5 g/l) of the oxidation catalyst.

The concentration of the refractory oxides, such as the solid solution of CeO_2 and ZrO_2, may be from 10% to 95% by weight of the oxidation catalyst, and alternatively, from 50% to 90%. This quantity may include any rare earth metal oxides added to the refractory oxides to enhance their capabilities. The concentration of the silica and/or tin oxide may be from 5% to 50%, and alternatively, 10% to 30%.

Depositing the catalyst material on the walls of the substrate, such as a honeycomb or monolithic structure, can be carried out by several processes. In one preferred process, the oxidation catalyst is washcoated onto the substrate. During the washcoating process, the refractory oxides, preferably stabilized with one or more rare earth oxides, silica and/or tin oxide, can be mixed together with water to form an aqueous mixture slurry. The aqueous mixture slurry may also contain a binder material. Suitable binder materials include, but are not limited to, colloidal alumina, colloidal silica, colloidal zirconia, colloidal ceria and conventional binders. The percentage of the binder in the aqueous mixture slurry can be in the range of 1-10%, by weight. Following the mixing of the components in the aqueous solution, the composition can be milled for a period from 1 to 24 hours to achieve a consistent composition and particle size. The substrate can be then coated with the aqueous mixture slurry and any extra slurry can be removed by air knifing or vacuum suction. After removing the extra aqueous mixture slurry, the coated substrate can be dried at a temperature of 100°C to 150°C for 8 hours followed by calcining at a temperature from 500°C to 600°C for 3 hours to secure the material to the substrate.

Following impregnation of the coated substrate with the mixture of materials, the platinum group metal components can be impregnated onto the coated substrate. In one preferred embodiment, this impregnation process can be accomplished by bringing the coated substrate into contact with an aqueous solution of the precious metal salts, preferably ruthenium and platinum salts alone or alternatively ruthenium or platinum salts and at least one other platinum group metal salt, using an incipient wetness impregnation process. In one embodiment, the preferred platinum salt is platinum nitrate and the preferred ruthenium salt is ruthenium nitrate. The coated substrate can be coated with the platinum group metal salts in an aqueous solution. It can be dried at a temperature from 100°C to 150°C and calcined at 300°C to 600°C preferably 300°C to 450°C for 3 hours.

The formation of the oxidation catalyst on the substrate can also be accomplished in a one step deposition and calcination process. In this process, the platinum group metal compounds can be added to the slurry of at least ceria and zirconia, preferably in the form of a solid solution, tin oxide and/or silica and a binder followed by milling, coating, drying and calcination steps.

Once the substrate is coated with the oxidation catalyst and calcined, it can be placed in the exhaust emission control device for oxidative destruction of CO and VOCs, particularly halogenated VOCs, including brominated VOCs. The exhaust gas, which contains CO and VOCs, including halogenated VOCs, contacts the catalyst, that is deposited on a monolith substrate, with an effective amount of oxygen at temperatures from 200°C up to 500°C and is oxidized into CO_2, water, and halogen-acid/halogens. The emission control device could be high or low pressure recuperative catalytic oxidizer, or a regenerative catalytic oxidizer. Because of the use of the catalyst deposited upon a monolith substrate, the catalyst has shown great utility even with low cell density ceramic monoliths.

The various catalyst embodiments of the invention typically have high activity for oxidation of these compounds. The light off temperatures for the destruction of these VOCs is typically lower than 250°C, as illustrated in Figure 1. This temperature is significantly lower than has been used with prior art catalysts.

The catalysts may operate at a gaseous hourly space velocity (GHSV) of 1000 - 100,000 h^{-1}, and alternatively from 5,000-50,000 h^{-1}, to achieve enhanced catalyst performance. The preferred space velocity can be obtained by increasing or deceasing catalyst volumes in the catalytic oxidation reactors.

The catalyst can operate within a large temperature window from 200°C up to 500°C, and alternatively from 250°C to 450°C, to achieve complete oxidation of CO and various VOCs which include halogenated organic compounds from chemical plant off-gas emissions with an effective amount of oxygen. This catalyst can be used effectively at lower temperatures and exhibits low pressure drop, such as is useful with a regenerative catalytic oxidizer. The amount of oxygen present depends on the quantity of VOCs that are present in the off-gas emissions. The range of operation temperatures can be controlled by injecting some assistant fuels, which are more easily volatilized organic compounds, into the off-gas exhaust stream. These assistant fuels are generally available in chemical plant processes and may include methanol,

ethanol, methyl-acetate, aromatic compounds, synthesis gas, nature gas and other similar organic compounds and mixtures thereof.

The catalyst can also be designed to operate in high pressure reactor systems, such as a high pressure catalytic oxidation unit. The working pressure can be from atmospheric to 300 psi (2.1 MPa), or alternatively, from 100- 200 psi. (0.6-1.4 MPa). The catalyst can also be designed to operate in low pressure reactor system, such as a low pressure recuperative oxidation unit or regenerative oxidation unit. For example, in PTA production application, the catalytic oxidation reactor can be installed before the off-gas expander for high pressure operations or after the off-gas expander for low pressure operations.

The catalyst can also be designed for use with low cell density monoliths.

The low cell density catalysts have shown special utility by spreading the reaction zone (the catalyst bed), across a larger total catalyst volume and bed depth, to match the low linear velocity designed into a regenerative catalytic oxidizer and yielding a combination of low temperature oxidation and low pressure drop.

This catalyst has also shown great durability with a productive life expectancy of at least three to five years.

EXAMPLES

The invention is further illustrated by the following examples:

Example 1.

A washcoat slurry (alternatively referred to as an "aqueous mixture slurry") is prepared by mixing 1000g of a La-doped ceria-zirconia powder (LCZ powder from Tianjiao Co. China), containing a solid solution of 23% zirconia and 72% ceria and 5% La_2O_3 with a surface area of 125 m^2/g and a single phase ceria cubic structure (see Figure 5), 150 g of silica (Davicat SI1203 from W.C. Grace) with 1.5 liters of water, followed by milling the mixture for 10 hours. A ceramic honeycomb substrate supplied by Corning having a diameter of 1.75 inches (4.45 cm), a length of 2inches (5.08 cm), and a cell density of 400 cells per square inch, cpsi, (62 cells per square cm) is dipped into the washcoat slurry. Extra slurry is blown out using an air-knife. The coated honeycomb is then dried at 120°C for 8 hours and calcined at 550°C for 3 hours. The resulting washcoat loading is 175g/l. A ruthenium nitrate/platinum nitrate solution is deposited on the coated substrate by an incipient wetness impregnation, followed by drying at 120°C for 8 hours and calcination at 400°C for 3 hours. The resulting loading is 2.1 g/l of ruthenium and 1.0 g/l of platinum. The performance of the catalyst is illustrated in Figure 1.

Example 2

A washcoat slurry is prepared by mixing 1000g of a solid solution of ceria and zirconia from Rhodia having 20% zirconia and 80% ceria and 150 g tin oxide from MEI (Magnesium Elektron Inc) with 1.5 liters of water, followed by milling the mixture for 10 hours. A ceramic honeycomb substrate supplied by Corning, having the same dimensions of the substrate described in Example 1 is dipped into the washcoat slurry. Extra slurry is blown out using an air-knife. The coated honeycomb is then dried at 120°C for 8 hours and calcined at 550°C for 3 hours. The resulting washcoat loading is 175g/l. A ruthenium nitrate/platinum nitrate solution is deposited on the coated substrate by an incipient wetness impregnation, followed by drying at 120°C for 8 hours and calcination at 550°C for 3 hours. The resulting loading is 2.2 g/l of ruthenium and 1.0 g/l of platinum. The performance of the catalyst is illustrated on Figure 2.

Comparative Example 3

A washcoat slurry is prepared by mixing 1000g of a solid solution of ceria and zirconia from Rhodia having 20%

zirconia and 80% ceria and silica from W.C. Grace with 1.5 liters of water, followed by milling the mixture for 10 hours. A ceramic honeycomb substrate supplied by Corning having the same dimensions as described in Example 1 is dipped into the washcoat slurry. Extra slurry is blown out using an air-knife. The coated honeycomb is then dried at 120°C for 2-3 hours and calcined at 550°C for 3 hours. The resulting washcoat loading is 175g/l. A ruthenium nitrate solution is deposited on the coated substrate by an incipient wetness impregnation, followed by drying at 120°C for 8 hours and calcination at 550°C for 3 hours. The resulting loading is 2.5 g/l of ruthenium. The performance of the catalyst is shown in Figure 3.

Comparative Example 4

A washcoat slurry is prepared by mixing 1000g of a solid solution of ceria and zirconia from Rhodia, having 20% zirconia and 80% ceria and silica from W.C. Grace with 1.5 liters of water, followed by milling the mixture for 10 hours. A ceramic honeycomb substrate supplied by Corning having the same dimensions of the substrate described in Example 1 is dipped into the washcoat slurry. Extra slurry is blown out using an air-knife. The coated honeycomb is then dried at 120°C for 8 hours and calcined at 550°C for 3 hours.

The resulting washcoat loading is 175g/l. A tetraammineplatinum nitrate solution is deposited on the coated substrate by an incipient wetness impregnation, followed by drying at 120°C for 8 hours and calcination at 550°C for 3 hours. The resulting loading is 1.24g/l of platinum. The performance of the catalyst is shown in Figure 4.

Example 5

A washcoat slurry is prepared by mixing 1000 g of ceria-zirconia powder obtained from Rhodia having a solid solution of 20% zirconia and 80% ceria with 150 g of silica from W.C. Grace along with 1.5 liters of water. The mixture was milled for 10 hours. A ceramic honeycomb substrate supplied by Corning having a diameter of 1.75 inches (4.45 cm), a length of 2 inches (5.08 cm) and a cell density of about 100 cpsi (15.5 cells per square centimeter) is dipped into the washcoat slurry. Extra slurry is blown out using an air knife. The coated honeycomb is then dried at a 120°C for 8 hours and calcined at 500°C for 3 hours. The resulting washcoat loading is 90g/l. A ruthenium nitrate/platinum nitrate solution is deposited on the coated substrate by an incipient wetness impregnation, followed by drying at 120°C for 8 hours and calcination at 400°C for 3 hours. The resulting loading is 1.1g/l of ruthenium and 0.40g/l of platinum. This catalyst could be used in a regenerative catalytic oxidation unit. The performance of the catalyst at low space velocity (9600 /hr) is illustrated in Figure 6.

The catalysts described above were tested in a laboratory reactor. The testing gas composition contained 3000 ppm CO; 250 ppm methyl-acetate, 20 ppm benzene, 20 ppm toluene; 50 ppm methyl bromide; 3% H_2O; 3% O_2 with the remaining portion being nitrogen. The test space velocity was 25,000 h^{-1}. The results are shown in Figures 1-4 and 6. A SRI8610C GC and NDIR CO analyzer was used for monitoring the oxidation reaction.

The results show that the various embodiments of the inventive catalysts are highly active for the oxidation of CO and various organic compounds, including halogenated organic compounds. From the test results, catalysts with both ruthenium and platinum showed a better performance for destruction of VOC and halogenated VOC (see Figures 1 and 2 and 6). When the catalyst only contained ruthenium as a precious metal, it exhibited a better performance for the halogenated VOC, methyl-bromide, but not for other VOCs (see Figure 3). When the catalyst only contained platinum as a precious metal, it showed a better performance for some VOC destruction but not for the destruction of halogenated VOC methyl-bromide (see Figure 4).

When using a low cell density monolith catalyst, such as example 6, the catalyst still show excellent VOC destruction performance at low space velocity.

Claims

1. An oxidation catalyst, deposited on a substrate, for the destruction of CO and volatile organic compounds, in particular halogenated organic compounds, from an emissions stream, wherein the oxidation catalyst comprises

at least two platinum group metals, one of which comprises ruthenium or platinum,

a refractory oxides support comprising a solid solution of CeO_2 and ZrO_2, wherein the refractory metal oxides comprise from 10% to 95%, by weight of the oxidation catalyst; and

one or both of silica and tin oxide and

wherein the substrate preferably has a honeycomb or monolithic structure and wherein the substrate is produced from the group consisting of cordierite, mullite, iron-chromium alloy and stainless steel.

2. The oxidation catalyst of Claim 1 wherein the two platinum group metals comprise ruthenium and platinum, and the ratio of ruthenium to platinum is 20 to 1 to 1 to 20.

3. The oxidation catalyst of Claims 1-2 wherein the refractory oxides support is stabilized by blending with one or more rare earth metal oxides selected from the group

consisting of lanthanum oxide, cerium oxide, yttrium oxide, praseodymium oxide, neodymium oxide, and mixtures thereof.

4. The oxidation catalyst of Claims 1-3 wherein the oxidation catalyst comprises tin oxide having a surface area from $2m^2/g$ to $200m^2/g$ and a particle size of from 1 to 20 micrometers, and the tin oxide comprises 5% to 50% of the oxidation catalyst.

5. The oxidation catalyst of Claims 1-4 wherein the platinum group metals are deposited on the substrate at a loading that comprises from 10 to 200 g/cf (0.35g/L to 7.1 g/L).

6. The oxidation catalyst of Claims 1-5 wherein the oxidation catalyst comprises silica, which comprises from 5% to 50%, by weight, of the oxidation catalyst, and the silica is selected from the group consisting of amorphous silica, precipitated silica, molecular sieves, MCM-41, SBA-15, and combinations thereof.

7. The oxidation catalyst of Claim 6 wherein the oxidation catalyst comprises silica comprising amorphous silica with a surface area more than 200 m^2/g, a pore size diameter greater than 100 angstrom and a particle size from 0.5-20 micrometers.

8. A process for the production of the oxidation catalyst deposited on the substrate of Claims 1-7 for the destruction of CO and volatile organic compounds, in particular halogenated organic compounds, from an emissions stream comprising

preparing an aqueous mixture slurry comprising a solid solution of CeO_2 and ZrO_2, one or both of tin oxide and silica to form a mixture and wherein the aqueous mixture slurry is blended with a binder selected from the group consisting of colloidal alumina, colloidal silica, colloidal titania, colloidal zirconia, colloidal ceria and mixtures thereof;

blending the mixture;

coating a substrate with the blended mixture;

drying and calcining the coated substrate;

depositing at least two platinum group metal precursor materials, comprising at least one of platinum and ruthenium, on the calcined coated substrate; and

drying and calcining the platinum group metals coated substrate.

9. A process for the production of the oxidation catalyst on the substrate of Claims 1-7 for the destruction of CO and volatile organic compounds, in particular

halogenated organic compounds, from an emissions stream comprising

depositing at least two precious metal precursors on at least one component selected from the group consisting of a solid solution of CeO_2 and ZrO_2, and one or both of tin oxide and silica to form a mixture;

blending the mixture;

coating a substrate with the blended mixture;

drying and calcining the coated substrate.

10. A method for treating a gas stream that contains CO and VOCs, including halogenated VOCs, and mixtures thereof, the method comprising

combining a gas stream that contains CO and VOCs, including halogenated VOCs, with oxygen; and

contacting the combined oxygen-gas stream with the catalyst on substrate of Claims 1-7 at a temperature from 200°C to 500°C.

11. The use of the oxidation catalyst of Claims 1-7 for destruction of volatile organic compounds, particularly halogenated organic compounds, from gaseous emission streams, particularly for use with high cell density substrates, such as 200-400 cpsi (30-60 cells per square centimeter)

substrate, for uses such as in a recuperative thermal oxidizer.

12. The use of the oxidation catalyst of Claims 1-7 for destruction of volatile organic compounds, particularly halogenated organic compounds, from gaseous emission streams, particularly for use with low cell density substrates less than 200 cpsi (30 cell per square centimeter) and particularly for substrates less than 100 cpsi (15 cells per square centimeter) substrates, for uses such as in a regenerative catalytic oxidizer.

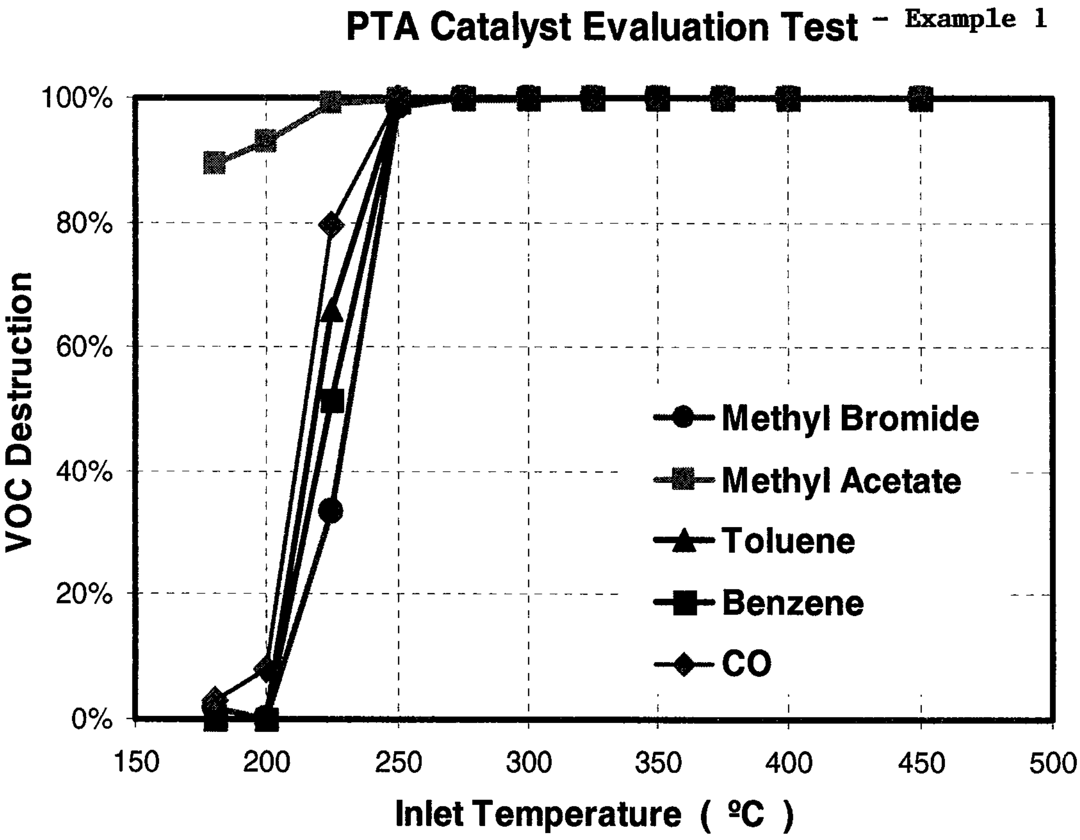

PTA Catalyst Evaluation Test - Example 1
VOC Destruction
100%
80%
60%
40%
20%
0%
150
200
250
300
350
400
450
500
Inlet Temperature (ºC)
Methyl Bromide
Methyl Acetate
Toluene
Benzene
CO

FIGURE 1

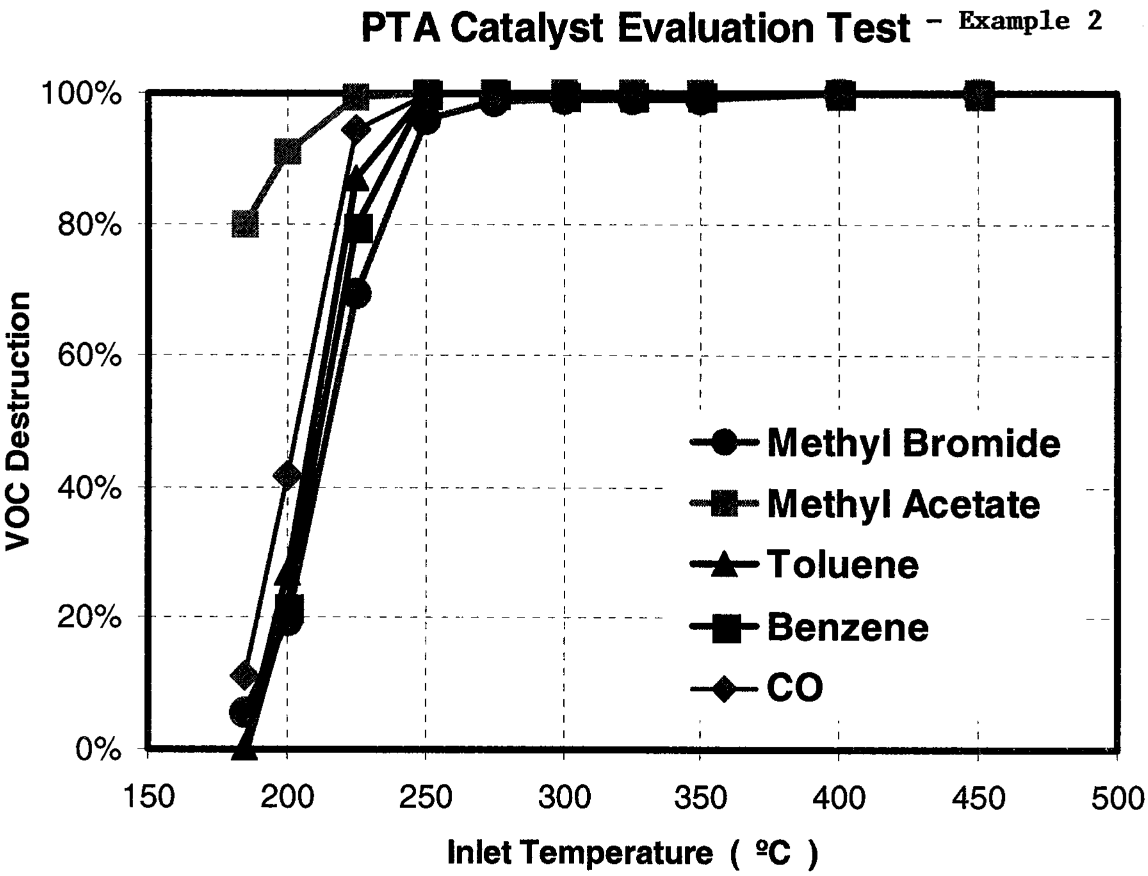

PTA Catalyst Evaluation Test - Example 2
VOC Destruction
0%
20%
40%
60%
80%
100%
Inlet Temperature (ºC)
150
200
250
300
350
400
450
500
Methyl Bromide
Methyl Acetate
Toluene
Benzene
CO

FIGURE 2

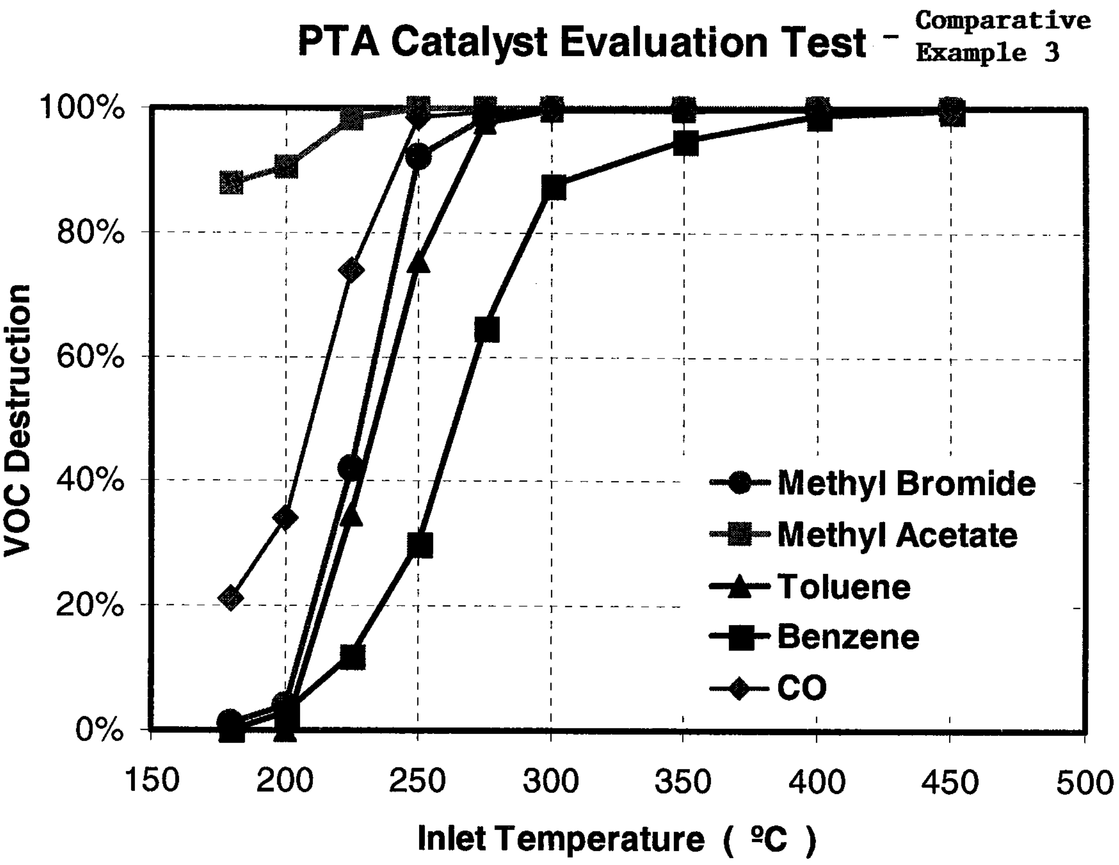

PTA Catalyst Evaluation Test – Comparative Example 3
100%
80%
60%
40%
20%
0%
VOC Destruction
150
200
250
300
350
400
450
500
Inlet Temperature (ºC)
Methyl Bromide
Methyl Acetate
Toluene
Benzene
CO

FIGURE 3

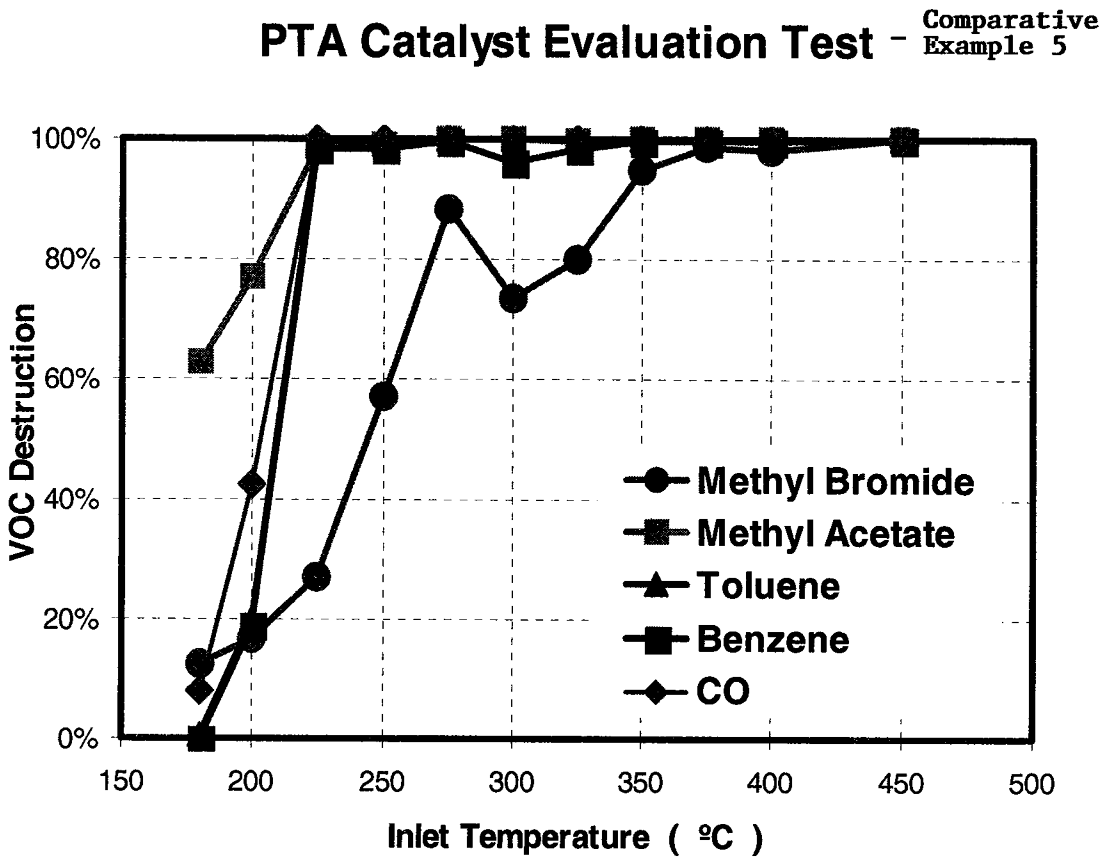
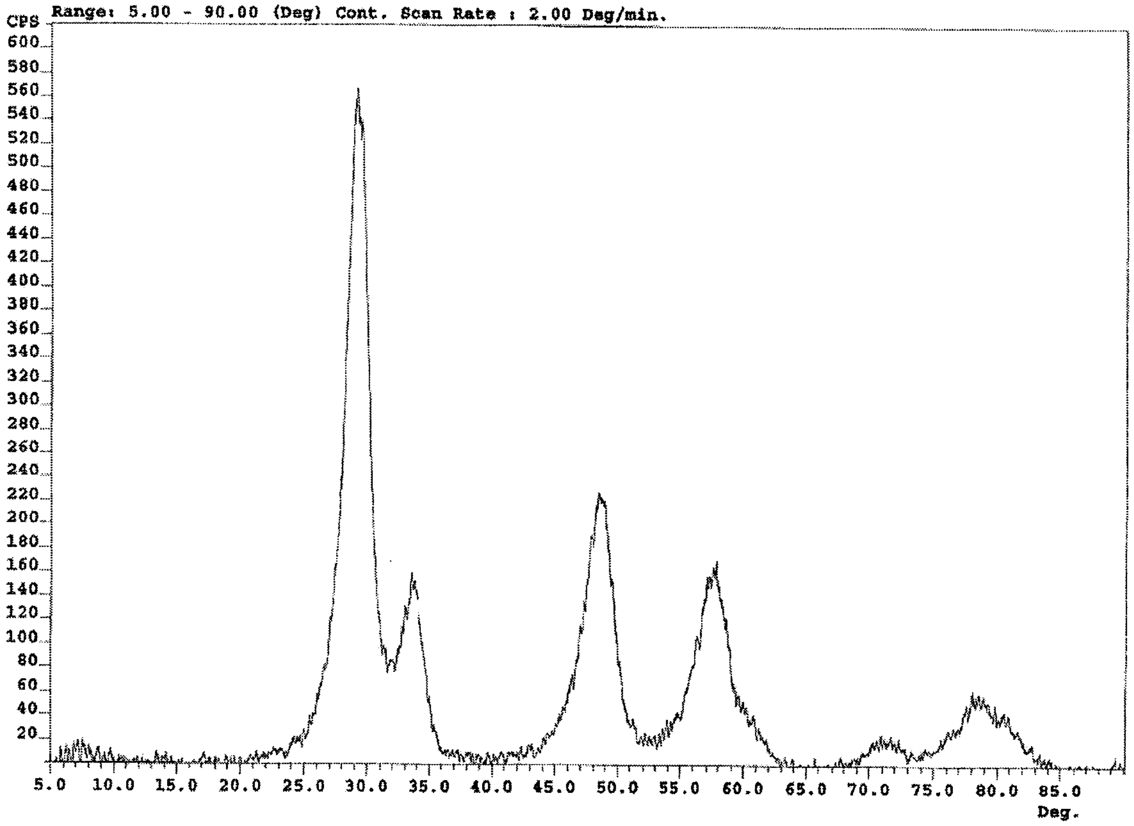

PTA Catalyst Evaluation Test - Comparative Example 5
100%
80%
60%
40%
20%
0%
VOC Destruction
150
200
250
300
350
400
450
500
Inlet Temperature (ºC)
Methyl Bromide
Methyl Acetate
Toluene
Benzene
CO

FIGURE 4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CPS
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560
540
520
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440
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180
160
140
120
100
80
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30.0
35.0
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80.0
85.0
Deg.

Figure 5.

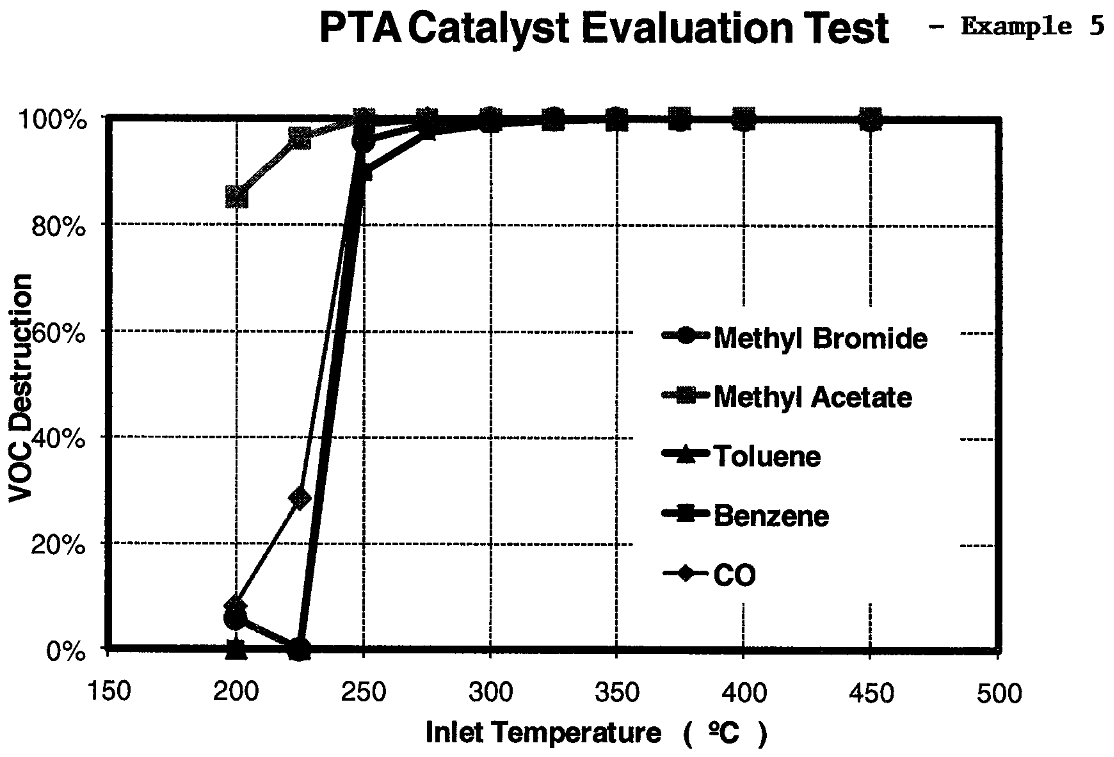
PTA Catalyst Evaluation Test - Example 5
100%
80%
60%
40%
20%
0%
VOC Destruction
Methyl Bromide
Methyl Acetate
Toluene
Benzene
CO
150
200
250
300
350
400
450
500
Inlet Temperature (ºC)

FIGURE 6