

NOBLE METAL-FREE CERIA-BASED DIESEL SOOT COMBUSTION CATALYST

P PATENTED TECHNOLOGY

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ABSTRACT

A new diesel soot combustion catalysts has been developed at the University of Alicante, which consists of high surface area ceria-praseodymia mixed oxide nanoparticles.

This technology is suitable for gas purification in diesel engine exhausts, like vehicles, stationary power generation engines, etc.

The research group is looking for companies interested in the utilization of this technology, either by licensing the patent, transfer of utilization rights, manufacture and commercialisation to third parties, I+D research project, etc.



INTRODUCTION

Important scientific and technical efforts in order to develop a device for soot removal in diesel engine exhausts, because these carbon nanoparticles are responsible of severe health and environmental negative effects. These devices usually consist of a filter located at in the exhaust pipe, where soot particles are collected, and a catalyst is usually used to lower the soot combustion temperature.

One of the main handicaps of these devices is the poor contact between soot and catalysts particles, which hinders significantly the catalyst performance. Platinum catalysts are the most active ones for this application among those with high enough stability under the demanding conditions of temperature and gas composition that are faced in an exhaust pipe. Alternative catalyst active phases are being investigated in order to lower the prize and improve the activity, and ceria-based oxides are promising candidates.

TECHNICAL DESCRIPTION

A catalyst active phase has been developed with the following composition:



particles size smaller than 9 nm and specific surface areas higher than 90 m²/g. The method used allows obtaining 7 nm particles with 125 m²/g surface area.

The synthesis is carried out using a reverse microemulsion and following the several steps:

1. The cerium and praseodymium precursors are dissolved in water.
2. An emulsion is prepared with the previous water solution.
3. Another alkali emulsion is prepared.
4. Both emulsions are mixed.
5. The solid obtained is separated by centrifugation.
6. The solid is calcined at T > 400°C.

Figure 1 shows the soot conversion profiles obtained with the novel ceria-praseodymia nanoparticles under a diesel exhaust simulated

gas mixture (500 ppm NO + 5% O₂ en N₂; 30000 h⁻¹). Reference curves obtained with a commercial 1% Pt/alumina catalyst, with a ceria-praseodymia prepared by a conventional precipitation procedure and without catalyst. All soot:catalyst mixtures used simulate the loose contact attained in real conditions.

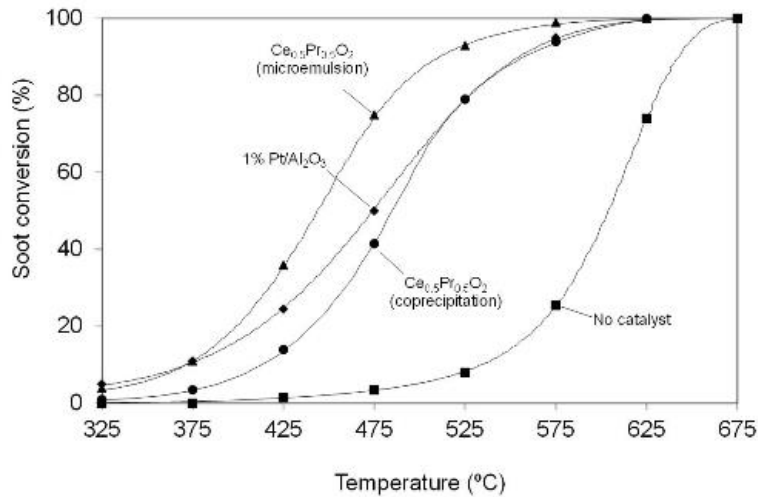


Figure 1

Figure 2 shows the relationship between soot combustion capacity and catalyst particle sizes/Surface area (under the experimental conditions of Figure 1) for ceria-based mixed oxides with zirconium of praseodymium. All catalysts were calcined at 500 °C, otherwise indicated.

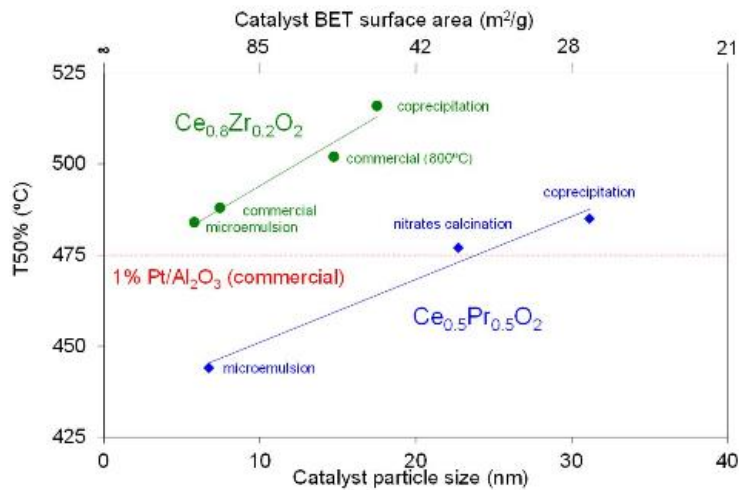


Figure 2

In order to provide a wider comparison, Table 1 compiles the T50% parameter, which is the temperature required for 50% soot conversion in the experimental conditions of Figures 1 and 2, for catalysts of very different formulation.

Tabla 1. Comparison of diesel soot combustion catalyst tested in realistic experimental conditions (loose soot-catalyst contact and NO_x+O₂ gas mixture):

| Catalyst [a] | T50% (°C) [b] |
|--|---------------|
| No catalyst | 607 |
| MnO | 601 |
| MnO ₂ | 597 |
| ZrO ₂ | 592 |
| TiO ₂ | 593 |
| CoAl ₂ O ₄ spinel | 563 |
| Cu/hectorite | 560 |
| Mn ₃ O ₄ | 510 |
| Ce _{0.8} Pr _{0.2} O ₂ (coprecipitation) | 502 |
| Ce _{0.8} Zr _{0.2} O ₂ (commercial) | 488 |
| Ce _{0.8} Zr _{0.2} O ₂ (microemulsion) | 484 |
| Ce _{0.5} Pr _{0.5} O ₂ (coprecipitation) | 484 |
| Cryptomelane | 481 |
| 1% Pt/CoAl ₂ O ₄ | 478 |
| 1% Pt/Al ₂ O ₃ (commercial) | 475 |
| Ce _{0.8} Pr _{0.2} O ₂ (microemulsion) | 459 |
| Ce _{0.5} Pr _{0.5} O ₂ (microemulsion) | 444 |

[a] The synthesis method of catalysts or if is commercial available is only indicated when relevant.
[b] temperature required for 50% soot conversion.

Doped ceria catalysts either with zirconium or praseodymium show high activity, but the platinum catalysts performance is on only overcome by the ceria-praseodymia catalysts prepared in the current invention by the microemulsion method. The high activity of these ceria-praseodymia catalysts is related to: (i) the intrinsic high catalytic activity of ceria-praseodymia mixed oxides, which relies on the high production of active oxygen species and (ii) the small particle size, which allows the transfer of such active oxygen species from catalyst to soot particles. This is evidenced on Figure 2, where the T50% temperature is plotted against the catalyst particle size for two sets of ceria-based catalysts. The selected compositions of these sets of catalysts were the most actives for ceria-zirconia (20 molar % zirconium) and ceria-praseodymia (50 molar % praseodymia) according to previous studies, and different synthesis methods were used (calcination of nitrates mixture, coprecipitation and reversed microemulsion; all catalysts were calcined at 500°C, otherwise indicated).

Figure 2 confirms that only the high surface area ceria-praseodymia catalysts prepared by reversed microemulsion are able to overcome the activity of the commercial Pt catalyst.

TECHNOLOGY ADVANTAGES AND INNOVATIVE ASPECTS

Better/equal activity than Pt catalysts at cheaper price.

CURRENT STATE OF DEVELOPMENT

The noble high surface area ceria-praseodymia catalysts have been tested at laboratory both as powder and supported on silicon carbide diesel particulate filters under simulated Diesel exhausts (with NO_x, O₂, H₂O, CO₂ y N₂).

MARKET APPLICATIONS

This technology is suitable for gas purification in Diesel engine exhausts, like vehicles, stationary power generation engines, etc.

COLLABORATION SOUGHT

Companies interested in the utilization of this technology, either by licensing the patent, transfer of utilization rights, manufacture and commercialisation to third parties, I+D research project, etc.

INTELLECTUAL PROPERTY RIGHTS

This technology is protected by a Spanish patent.

- Request number: 201400533
- Request date: 02/07/2014

MARKET APPLICATION (3)

Pollution and Environmental Impact
Chemical Technology
Transport and Automotive