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Nanoparticles, Catalyst,
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DPF

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NONOPARTICLES MATERIALS IN DIESEL PARTICULATE FILTERS

The reduction of platinum (Pt) loadings in the catalytic bed constitutes a primary means of reducing cost to the levels required for mass- produced vehicles. We have produced and tested, on the laboratory scale a series of innovative catalysts as an active part of a new PM- filter consisting of Pd-Au-Ag-Ni-Co (non Pt) nanometric, powder alloy. The hollow part structure of TiO_{2-x}-RuO_{2-x} *has been proposed as the active layer on the catalyst support, composed of SiC. We have previously demonstrated that single layers of Pt atoms on some other materials, such as palladium (Pd) or gold- nickel alloys, have higher activities than the analogous all-Pt catalysts. Such control of the composition and structure of the top-most atomic layers of catalyst particles gives hope of achieving the four-fold increase in mass activity catalysts needed to reach automotive catalyst cost targets.*

1. INTRODUCTION

The price of the catalyst is one of the main barriers to the development of affordable fuel cells and automotive catalyst bed and DPF.

However, platinum is a very costly noble metal material, and alternatives are needed to reduce the cost for practical application of automotive catalysts and fuel cells.

A very active area of development in the DPF field is optimization of the system.Palladium is a member of the platinum group of metals. It shares many of the chemical properties of platinum. Like platinum, it is used in catalytic converters for cars and for other catalysts that make use of its properties. In short, palladium is a highly useful and highly valued metal.

The role of the surface structure for the catalytic activity of a metal surface is studied using density functional theory. Monatomic steps at close packed Ru and Pd surfaces are identified to be highly reactive for the dissociation of diatomic molecules (NO, CO, N_2). The high reactivity is caused by the existence of a favorable reaction ensemble at which the complex reaction (e.g. stretched NO) coordinates to surface metal atoms [8].

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Recent theoretical work showed that the coverage of O on Ru (0001) is not limited to=0:5ML, which was for a long time believed to be the saturation coverage under UHV conditions [8]. Subsequent experiments indicated an exceptionally high catalytic activity of the Ru (0001) surface (compared to other Pd group transition metals), when high loads of O are stored not only on, but also inside the sample. In these experiments it was also observed that such surfaces are severely destabilized, leading to RuO_2oxide formation and to RuO_x (x=4) fragmentation at elevated temperatures [8]. We performed density functional theory calculations to gain an understanding of the nature of the O-Ru bonds and of the ensuing destabilization, when Ru is loaded with oxygen coverages between 0-2ML. After a full O monolayer is completed on the surface, O starts to penetrate into Ru(0001), yet preferring to stay directly below the substrate layer and not deeper. We observe a tendency to form sub-surface islands, where the thus formed O-Ru-O surface is only loosely connected to the underlying substrate and may be considered as a precursor to oxide formation.

RuO_2 is one of the most widely applied oxide-catalyst materials owing to its high chemical stability, lower cost than Pt and good flexibility in fabrication. Such RuO_2 nanomaterials are especially attractive due to their tunable electronic and optoelectronic properties.

2. EXPERIMENTAL

The aim of this study was to clarify factors which may improve catalytic properties and reduce the cost for PDF.

Two points of view were presented: method of deposition of ruthenium catalyst on monocrystalline rutile and method of deposition of nanocluster TiO_2-RuO_2 on catalytic bed. Ruthenium were deposited by Pulsed Magnetron Sputtering on (100) plane of TiO_2 (rutile) single crystal. It was found that surface defects of single crystal plane considerably influence on ruthenium crystallites growth. The ruthenium films were annealed in oxygen atmosphere in temperature range of 380-800 ° C during 4-48 h.

This process leads to partially oxidation of ruthenium and formation bilayers coating of RuO_{2-x}/Ru. Nanoparticles with high purity and relatively narrow size distribution can be synthesized efficiently by thermal aerosol synthesis. [2]. Investigation of nanostructural of probes TiO_2-RuO_2 , which were obtained by USPD were described in patent No. PL 195839.

In conventional spray pyrolysis, the solution is atomized into a hot wall reactor where the aerosol droplets undergo evaporation, drying and thermolysis of the precipitate particles at higher temperature to form a microporous particle and eventually, dense particles by sintering.

PDF catalyst TiO_2-RuO_2 was obtained by Flame Synthesis. The precursor solutions consisted of titanium (Isopropoxide (97%, Aldrich) and $RuCl_2$ dissolved in an Isopropyl-Alcohol 20 vol%.

The liquid precursor mixture is rapidly dispersed by a gas stream of oxygen and ignited by a premixed methane/oxygen flame.

Flame aerosol synthesis, one of the most promising routes applicable to manufacture of a range of single and multi-component functional nanoparticles at low cost and with high production rates, refers to the formation of fine particles from gases in flames [1]. Today, flame technology is employed routinely in large scale manufacture of carbon blacks and metal oxide commodities such as fumed silica and pigmentary titania and, to a lesser extent, for specialty chemicals such as zinc oxide and alumina powders. Zinc oxide (ZnO) is the third largest flame-aerosol-made material after carbon black and pigmentary titania with global consumption of 600,000 t/y [1].

The size of the particles ranges from a few to several hundred nanometers in diameter, depending on the material and process conditions [2]. Nanoparticles with high purity and relatively narrow size distribution can be synthesized efficiently in flame aerosol reactors [2]. These reactors are routinely used in industry to make a variety of commodities by combusting halide and hydrocarbon vapors. On the other hand, combustion of sprays is quite attractive as it can utilize a broader spectrum of liquid precursors than conventional vapor flame reactors. Combustion of liquid precursor droplets has been used also in synthesis of mixed oxide powders by the so-called flame spray pyrolysis (FSP) process. The FSP process was systematically investigated using an external-mixing gas-assisted atomizer supported by premixed methane and oxygen flamelets [2]. The FSP is capable of producing mixed metal oxide powder in the 1-200 nm size range from low-cost precursors with production rates of up to 250 g/h.

AFM measurements were performed to study the differences on the surface morphology of sample prior to catalyst bed fabrication. Atomic Force Microscopy (AFM) analysis the ruthenium film of 400 nm thickness. The micrographs of sample is presented in Figures 1, respectively, over scales of 200 nm x 400 nm. The ruthenium film obtained by PVD technique has agglomerated particles. Here it has been observed that the samples had agglomerated particles. The average grain sizes of ruthenium were found to be almost in the same range of 30-400 nm.

This result can be explained as follows: during the formation TiO_2-RuO_2 and deposition on the SiC-Al_2O_3 filters, processes in the flame, the TiO_2-RuO_2 created a new nucleation centers, which in turn changed the nucleation type from homogeneous to heterogeneous.

SiC has very high thermal conductivity and mechanical strength. The cracking problem during regeneration could be successfully handled by using split- type DPFs that consist of multiple filter segments. For enhancing further durability of SiC-DPF, increasing the regeneration limit was successful by means of increasing a volume of the neck area located between SiC particles. The improvement was probably due to the lowering of Young’s modulus and increasing of thermal shock fracture resistance parameter R’, which were results of increasing the neck volume and controlling the sintering method. Crack propagation mode changed from conventional mode, and the crack propagating throughout the whole tended to be restrained. Nevertheless, the TiO_2-RuO_2 dispersion, the TiO_2-RuO_2 sizes and the accurate size of particle can be determined by TEM, and HRTEM measurements.

Figure 2 shows HRTEM bright-field images of samples TiO_2-RuO_2 with different magnifications. The corresponding diffraction patterns are shown in the insets. Figure 3(a) show the bright-field images of the FSP made nanoparticles, which were polyhedral aggregated of primary particles. Figure 3(a-b) HREM shows the morphologies of flame made colony of TiO_2-RuO_2 nanoparticles containing mainly spheroidal particles typically with diameters ranging from 50-500 nm. Figure 3 (c-e) HREM gives the EDS elemental composition signal. Point 1 emphasized clearly a signal corresponding to Ti and Ru. Figure 4(a) shows the morphologies of TiO_2-RuO_2 flame made sphere. Nanocrystalline sphere, which is showed in Figure 4 contains nanocluster in the size 5 nm.

Figure 4(b-c) gives the EDS elemental composition signal. Point 1 emphasized clearly linescape analysis corresponding to Ti and Ru. Figure 5 shows the crystal defects of TiO_2-RuO_2 flame made sphere. The defects are the most severe ones affecting the structural properties of TiO_2-RuO_2.

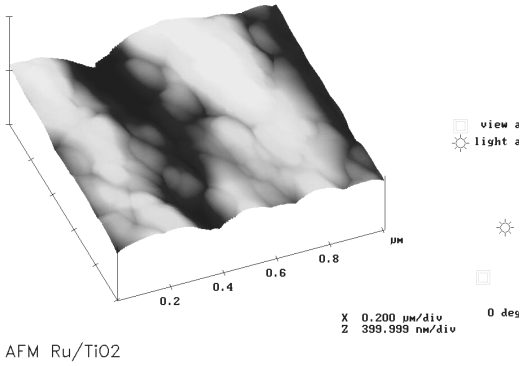

Fig. 1. AFM micrographs of the surface of the ruthenium bilayers on the TiO_2-rutile single crystals

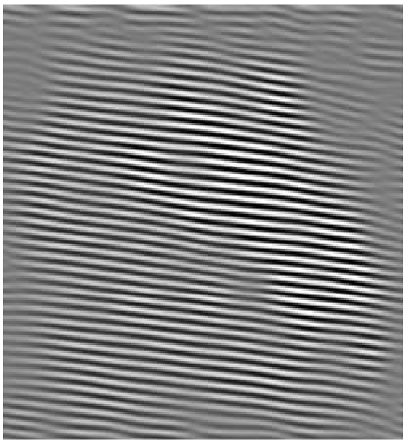

Fig. 2. HRTEM images of TiO_2-RuO_2 samples

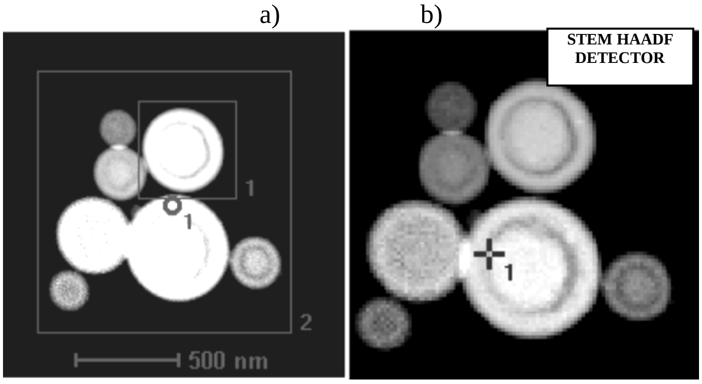

Fig. 3(a, b). HREM shows the morphologies of flame made colony of TiO_2-RuO_2

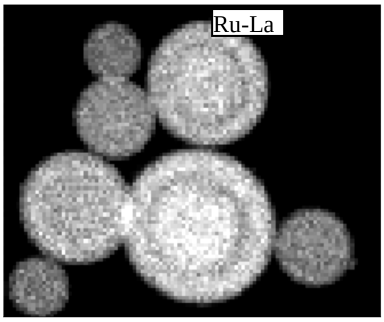

Fig. 3(c). HREM gives the EDS elemental composition signal corresponding to Ru

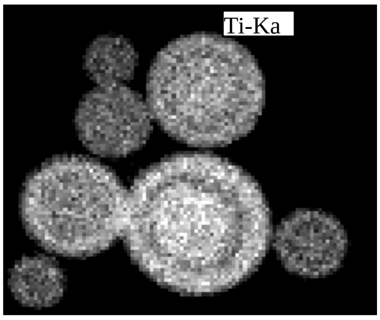

Fig. 3(d). HREM gives the EDS elemental composition signal corresponding to Ti

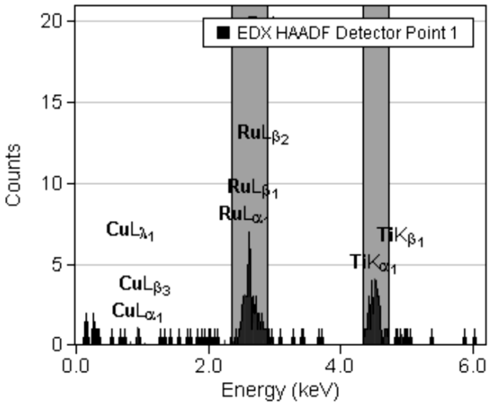

Fig. 3(e). HREM gives the EDS elemental composition signal to Ti and Ru

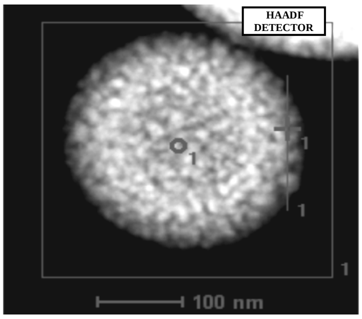

Fig. 4(a). The morphologies of flame made sphere of TiO$_2$-RuO$_2$

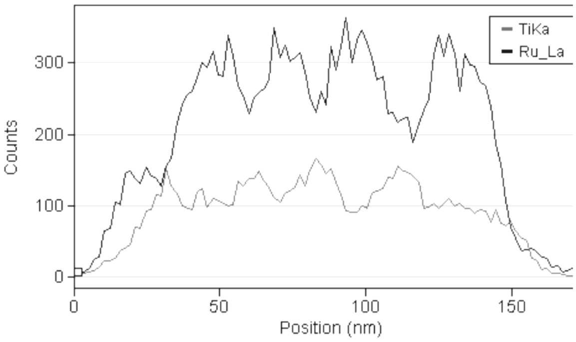

Fig. 4(b). The EDS linescape analysis corresponding to Ti and Ru

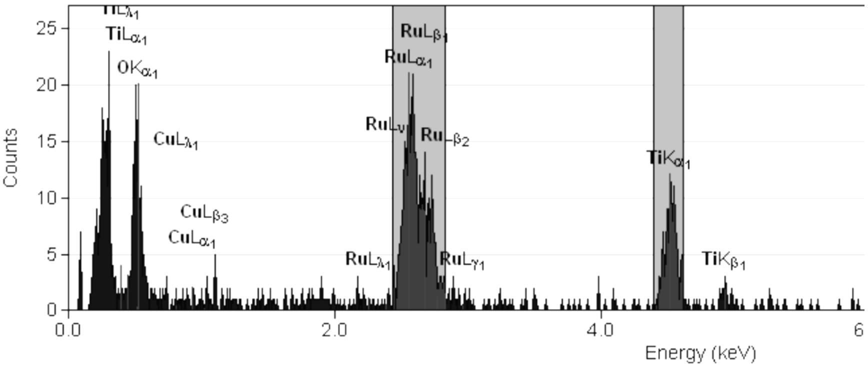

Fig. 4(c). The EDS linescape analysis corresponding to Ti and Ru

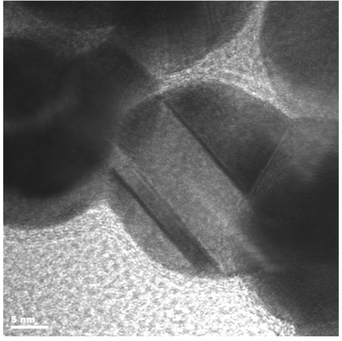

Fig. 5. HREM crystal defects of flame made sphere of TiO_2-RuO_2

3. CONCLUSION

TiO_2-RuO_2 is active part of the second generation catalyst bed of DPF. Non agglomerated sphere will be used in particulate filter in Biodiesel car. RuO_2 on single crystalline substrates of rutile, exhibits catalytic high activity. Defect structure of flame made sphere -TiO_2-$RuO_{2,}$ which was given by HREM, permits to gain active substrate for DPF.

4. REFERENCES

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