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Ceria-supported small Pt and Pt_3Sn nanoparticles for NO_x-assisted soot oxidation

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ABSTRACT

Introduced herein are small Pt and Pt_3Sn nanoparticles, stabilized with organosilane or organostannane and impregnated on ceria support, as active sites for NO_x-assisted soot oxidation reaction. The catalysts have been tested with four reactions: CO oxidation, NO oxidation, NO_x-free soot oxidation and finally NO_x-assisted soot oxidation. Our Pt nanoparticles reportedly possess remarkable catalytic activities in CO oxidation, as they actively convert CO at 50 °C, while the alloy Pt_3Sn nanoparticles are active at higher temperature. The Pt nanoparticles also mediate more actively NO oxidation than their alloy counterpart, leading to more NO_2 production beneficial for soot oxidation. The influence of Pt and Pt_3Sn active sites on the catalytic activity during NO_x-free soot oxidation becomes less prominent than the morphology, due to the high dependency of the reaction on catalyst structure. The presence of Sn, nevertheless, induces lower oxidation reaction temperature. Finally, in the presence of NO_x, the metal active sites undoubtedly boost the catalytic activity of soot oxidation. Pt/CeO_2-NC (NC stands for "nanocubes"), reported herein as our most achieving catalyst, demonstrates a remarkable activity, lowering the oxidation temperature at about 80 °C, thanks to the synergy of the active metal nanoparticles and reactive ceria nanocubes. Surprisingly, the catalytic activity of the alloy counterpart (Pt_3Sn/CeO_2-NC) is close to Pt/CeO_2-NC, indicating the potential of the catalyst as an alternative to reducing the employment of precious metal in automotive catalysis. The thermally aged Pt catalysts have demonstrated good resistance to sintering, thanks to the outer protection by silica patches. However, the catalytic activities of the aged Pt_3Sn catalysts rely heavily on support morphology.

1. Introduction

Diesel exhaust gas aftertreatment technology has been experiencing years of developments. New challenges for current car manufacturers have emerged since the enforcement of Euro VI, in which emissions of particulate matter (PM) and nitrogen oxides (NO_x) must be reduced till 0.005 and 0.08 g km^{-1}, respectively [1]. Obsolete reduction technologies involving modifications in an internal combustion engine are no longer efficient in yielding very low pollutant emissions. Therefore, downstream pollutant abatement involving approaches from chemistry and catalysis must unavoidably be taken.

Particulate matter (PM), more colloquially called "soot", has been an ongoing issue in developing Diesel engine vehicles due to its detrimental impact on respiratory system [2]. Constituted mainly of carbonaceous compounds, soot can solely be abated via oxidation reactions. Due to its solid nature, soot is normally treated in two steps: filtration and regeneration. The former refers to the entrapment of soot in a Diesel Particulate Filter (DPF); a porous, monolithic structure that enables wall-flow filtration [3,4]. The latter refers to the cleanup of soot-laden filter via combustion in order to avoid the entailing backpressure. Regenerating filter is a demanding task as oftentimes the reaction condition may become too extreme. In a conventional fashion, the regeneration is carried out in "active" mode [5–7], which requires active participation from oxygen, active thermal induction coming from Diesel Oxidation Catalyst (DOC), and a catalytic washcoat. The reaction between soot and oxygen, even mediated with catalysts, occurs effectively at above 550 °C [3,6,7]. The exothermicity of the reaction, however, could raise the overall temperature up to 1000 °C, inflicting structural damage to the filter. The contemporary approach, known as "passive regeneration" [6–8], involves NO_x as the third reagent,

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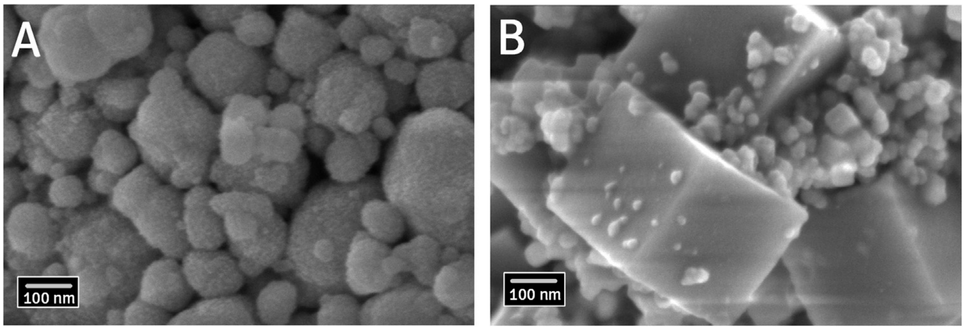

Fig. 1. FE-SEM images of catalyst's supports: (A) CeO_2-SCS and (B) CeO_2-NC.

thanks to its abundant presence in Diesel exhaust gas stream. This NO_x-assisted reaction benefits from the strong oxidizing nature of NO_2, with which soot combustion is expected to occur at lower temperature. Two major components constituting a perfect catalyst for passive regeneration are: (1) an oxide support and (2) an active oxidation catalyst

Cerium dioxide (CeO_2), casually known as "ceria", has been popular amid global researchers for its ability to undergo rapid reduction and oxidation (its so-called "redox properties") and to have outstanding oxygen storage capacity (OSC), therefore it is frequently studied as the potential oxide support [9–15]. Many researchers have been investigating the effect of various physicochemical properties of ceria in order to obtain not only better soot oxidation [16–23] but also better CO and propane oxidation [24]. Tailoring the right morphology of ceria, in particular, could induce high catalytic activity, as catalytic soot oxidation strongly necessitates a good interaction between soot, a solid reactant, and the solid-phase catalyst [25,26]. Interestingly, various shapes often give different reactivity towards the reaction, especially in the nanoscale level. Previous research, taken as examples, have demonstrated that well-defined ceria nanocubes and nanorods enhance soot oxidation activity compared to ceria nanopolyhedra, owing to their reactive, rather unstable (100) and (110) planes [16,17,19].

Platinum-Group Metals (PGMs) are broadly used as active oxidation catalysts. Besides their remarkable activities for any oxidation reactions, PGMs are still preferred because of their resistance to corrosion. Platinum (Pt), in particular, has been employed in many automotive catalytic processes, starting from Diesel Oxidation Catalysts (DOC) [27,28], the early generation of catalytic converters, to Three-Way Catalysis (TWC) [29] for abating simultaneously CO, hydrocarbons and NO_x emissions through oxidation-reduction cycles and the most recent Lean NO_x Trap (LNT) [30,31], in which NO_x are periodically trapped and reduced to N_2. The activity of Pt-containing phase relies much on its particle size; the smaller the size, the better the oxidation activity [32,33]. However, since automotive catalysis normally runs at high temperatures under oxidative atmosphere, Pt often suffers from sintering – particle enlargement via diffusion/agglomeration or ripening process [34–36]. As the particle loses its active sites, sintering leads to catalyst deactivation. Stabilized Pt nanoparticles are an alternative to the conventional, large Pt clusters and they are prepared via an organometallic synthesis [37–39]. Pelzer et al. have successfully obtained small (±2 nm) Pt(0) nanoparticles, stabilized with *n*-octylsilane via direct Pt_3Si bonds [38]. The silyl ligands not only help prevent Pt nanoparticles from agglomeration during particle growth but also keep them from sintering when they are already impregnated onto a support.

Commercialization of Pt-based automotive catalysts, however, remains an issue due to the prohibitive price of the metal. A possible alternative to this might be a dilution of Pt with non-noble metals. Interestingly, the alloy Pt_3Sn can be prepared through the same organometallic synthesis [40]. Boualleg et al. have observed an unexpected formation of Pt_3Sn nanoparticles after contacting Pt and Sn precursors $[Pt(dba)_2$ (dba = dibenzylideneacetone) and $(n\text{-}Bu)_3Sn\text{-}H]$ under H_2 at room temperature without using other stabilizing ligands [40].

The present work reports such small Pt and Pt_3Sn nanoparticles impregnated onto ceria nanocubes (prepared via a hydrothermal synthesis) as a new means of mediating low-temperature NO_x-assisted soot abatement. Four reactions have been carried out to shed light on the performances of the prepared catalysts: (1) CO oxidation as an intermediate reaction in the mechanism of soot oxidation; (2) NO oxidation as the reaction that helps understand the functionality of Pt nanoparticles in producing NO_2; (3) regular soot oxidation under oxygenic atmosphere as the core reaction in the present study; and eventually (4) soot oxidation in the presence of NO_x. Another ceria support, synthesized through solution combustion technique, has also been used for comparison. This work is finally completed with several catalyst characterizations.

2. Experimental

2.1. Catalyst preparation

Two cerium dioxide supports, namely CeO_2-SCS (SCS = solution combustion synthesis) and CeO_2-NC (NC = nanocubes) have been prepared through solution combustion and hydrothermal syntheses respectively. In a typical SC synthesis, $Ce(NO_3)_3{\cdot}6H_2O$ (4 mmol, Sigma-Aldrich) and $CO(NH_2)_2$ (10 mmol, Sigma-Aldrich) are dissolved in 60 ml of deionized H_2O. The solution is then transferred into a ceramic crucible, heated in a furnace at 650 °C for 20 min. On the other hand, a typical hydrothermal synthesis requires precipitating 0.01 mmol of $Ce(NO_3)_3{\cdot}6H_2O$ (0.01 mmol) with NaOH (1.2 mol, Sigma-Aldrich), in 80 ml of deionized water. The violetish-white slurry resulting from the precipitation is then transferred into a 200-ml autoclave, heated at 180 °C for 24 h. The clear white precipitate is rinsed with ethanol and deionized water, separated from the washing liquid in a centrifuge and dried overnight at 70 °C. The final dried precipitate is calcined at 550 °C for 4 h.

In the synthesis of the Pt and Pt_3Sn nanoparticles, $Pt(dba)_2$ is used as the precursor and prepared according to the literature [41]. Pt nanoparticles were obtained as a dark brown colloid (0.05 mmol) by contacting $Pt(dba)_2$ (0.05 mmol) and $Si(n\text{-}C_8H_{17})$ (Sigma-Aldrich) (0.05 mmol) in dry THF (34 ml) in a Schlenk flask under Ar which is then transferred to a high-pressure glass reactor for a reaction under 3 bar of H_2. Pt_3Sn nanoparticles (0.04 mmol) were obtained likewise by contacting $Pt(dba)_2$ (0.04 mmol) with $(n\text{-}Bu)_3Sn\text{-}H$ (Sigma-Aldrich) (0.04 mmol, excess), in dry THF (28 ml). The excess of Sn, in the synthesis of Pt_3Sn nanoparticles, is removed by three-time washings with dry pentane, followed by cryogenic precipitation and decantation (liquid nitrogen as coolant).