



# Catalytic performance of supported Ag nano-particles prepared by liquid phase chemical reduction for soot oxidation



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## ABSTRACT

The effect of size and morphology of Ag catalysts supported on ZrO<sub>2</sub> on the soot oxidation activity was investigated. Spherically shaped Ag nano-particles with the size of ca. 16 nm, prepared by liquid-phase chemical reduction, supported on ZrO<sub>2</sub> (Ag/ZrO<sub>2</sub>(NP)) exhibited outstanding performance for soot oxidation with gaseous O<sub>2</sub> in tight and loose contact modes, compared with hemispherically shaped Ag particles prepared by impregnation (Ag/ZrO<sub>2</sub>(IMP)). The exceptional performance of Ag/ZrO<sub>2</sub>(NP) for soot oxidation in loose contact mode was explained by relatively good catalyst-soot contact state and effective migration of active oxygen species from the catalyst to soot. In addition to morphological effect, Ag nano-particles supported on ZrO<sub>2</sub> were found to be stabilized in the surface valence state of Ag<sup>+</sup>, and then oxygen species participating in soot oxidation can be effectively activated on Ag<sup>+</sup> sites. We concluded that the presence of Ag<sup>+</sup> sites on the surface of Ag nano-particles is responsible for high soot oxidation activity.

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## 1. Introduction

Diesel particulate filter (DPF) can effectively remove particulate matter (PM) emitted from diesel engines. Soot, which is the main component of PM, trapped in a DPF must be periodically removed by combustion to prevent the filter from becoming clogged with soot. Although the direct oxidation of soot by O<sub>2</sub> needs high temperatures around 600 °C, the use of catalysts is well known to effectively decrease the temperature required for DPF regeneration, leading to an increase in the overall fuel efficiency of the diesel engine.

Numerous amounts of catalysts, ranging from noble metals to metal oxides, were so far reported to show activity for soot oxidation [1,2]. For example, platinum can catalyze effectively soot oxidation [3,4]. Its catalytic performance is, however, strongly dependent on the reactant gas composition. Oi-Uchisawa et al. [5,6] reported that Pt catalyst supported on SiO<sub>2</sub> showed higher soot oxidation activity in the condition of NO + O<sub>2</sub> + N<sub>2</sub> than without NO. This was explained by the participation of NO<sub>2</sub>, which was formed by oxidation of NO on Pt, as strong oxidant for soot

compared with O<sub>2</sub> [6,7]. Makkee et al. [8,9] observed the acceleration of NO<sub>x</sub>-assisted soot oxidation reaction over Pt/Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> combined catalysts and reported that the interaction of NO<sub>2</sub>, which is formed on Pt/Al<sub>2</sub>O<sub>3</sub>, with CeO<sub>2</sub> causes the oxygen transfer to CeO<sub>2</sub> surface, and the active oxygen thus formed plays an important role in the soot oxidation. The essential role of CeO<sub>2</sub> is suspected to be due to high oxygen storage performance. In fact, Machida et al. [10] revealed that CeO<sub>2</sub> can catalyze soot oxidation by O<sub>2</sub> and that oxygen species formed from the gaseous O<sub>2</sub> and/or the lattice oxygen at the CeO<sub>2</sub>/soot interface contributes to the soot oxidation. The participation of lattice oxygen in metal oxide catalysts in soot oxidation by O<sub>2</sub> was also demonstrated from the extensive investigation using composite oxide materials with high oxide ion conductivities such as Zr<sub>0.8</sub>Y<sub>0.2</sub>O<sub>2-x</sub> and Zr<sub>0.7</sub>Nd<sub>0.3</sub>O<sub>2-x</sub> [11]. Although CeO<sub>2</sub> and oxide ion conductors are one of the candidates for soot oxidation by O<sub>2</sub>, these catalysts show activity at relatively high temperature around 400–520 °C because the mobility of lattice oxygen is an important factor to determine the catalytic performance.

The use of metal-doped oxide catalysts can increase the benefit of bare oxide due to the establishment of an interaction between doped-metal and support oxide. Among the metal additives investigated so far, Ag is one of the attractive active components, which can catalyze soot oxidation by O<sub>2</sub> at low temperatures [12–15]. Aneggi et al. [16] systematically studied the effect of Ag

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catalysts supported on various metal oxides on the catalytic performance for soot oxidation and found that not only Ag/CeO<sub>2</sub> but also Ag/ZrO<sub>2</sub> shows high soot oxidation activity with the effective temperature region around 300 °C. They suggested that Ag species in a zero valent state on ZrO<sub>2</sub> are catalytically active species. Nanba et al. [17] investigated the effect of particle size of Ag supported on ZrO<sub>2</sub> for soot oxidation by O<sub>2</sub> and revealed that the catalytically active Ag species are nanoparticles having a particle size of 2–10 nm. They also characterized in detail the active oxygen species on Ag active sites of Ag/ZrO<sub>2</sub> catalysts. From the comparison of CO<sub>2</sub> formation profile in soot oxidation and N<sub>2</sub>O formation profile in temperature-programmed reduction by NH<sub>3</sub> (NH<sub>3</sub>-TPR), oxygen species in the neighbor of interface between Ag and ZrO<sub>2</sub> was proposed to be the active oxygen species for soot oxidation [18].

Since soot oxidation on catalyst takes place at three-phase boundary between soot (solid), catalyst (solid) and O<sub>2</sub> (gas), the particle size and morphology of catalytically active Ag species is considered to be an important factor determining the soot oxidation activity. In the present study, we have prepared Ag nano-particles with different size and morphology by liquid-phase chemical reduction and impregnation methods. The effect of size and morphology of Ag catalysts on the soot oxidation activity was investigated.

## 2. Experimental

Ag nano-particles supported on ZrO<sub>2</sub>, denoted as Ag/ZrO<sub>2</sub>(NP), was prepared by liquid-phase chemical reduction method as follows [19]. Silver(I) nitrate (AgNO<sub>3</sub>) was first dissolved in distilled water and agitated for 1 h, followed by addition of trisodium citrate and ZrO<sub>2</sub> powder (Toso, TZ-0, 14 m<sup>2</sup> g<sup>-1</sup>). Sodium borohydride (NaBH<sub>4</sub>) as the reducing agent was added to the solution mentioned above, and the solution was then stirred at room temperature. The ZrO<sub>2</sub> powder deposited Ag nano-particles thus obtained was washed with distilled water and subsequently with ethanol, followed by drying at 110 °C for 24 h in air. Ag/ZrO<sub>2</sub>(NP) was not calcined at high temperature in air to avoid aggregation of Ag nano-particles before activity test. Ag/ZrO<sub>2</sub>(IMP) was prepared by impregnation of ZrO<sub>2</sub> (Toso, TZ-0) with a solution of AgNO<sub>3</sub>, followed by drying and calcination at 600 °C for 5 h in air. The Ag loading was fixed at 10 wt%.

The catalytic activity for soot oxidation was determined using commercially available carbon black powder (Aldrich), which was found to be an aggregate composed of 20–40 nm carbon particles by TEM observation, as model diesel soot. The carbon black and catalyst with a weight ratio of 1/19 were mixed under different conditions, obtaining, so-called, tight contact and loose contact states. In case of tight contact, the catalyst and carbon black powder were well mixed in an agate mortar for 10 min. The loose contact was achieved by mixing catalyst with carbon black with a spatula for 5 min. The activity was evaluated with a flow reactor system by passing a reactant gas containing 10% O<sub>2</sub> diluted in He at a rate of 50 cm<sup>3</sup> min<sup>-1</sup> over 40 mg of a mixture. The temperature was increased to 700 °C at a rate of 2 °C min<sup>-1</sup>. The concentration of CO and CO<sub>2</sub> as a product was measured with on-line gas chromatograph (Shimadzu GC-2014ATTF). No formation of CO was observed in the present study.

Isotopic transient kinetic analysis was performed by switching the flowing gas from 1% <sup>16</sup>O<sub>2</sub> to 1% <sup>18</sup>O<sub>2</sub> diluted in Ar at 320 °C. 40 mg of a mixture of the carbon black and catalyst in tight contact mode was employed. The effluent gas from the reactor was continuously monitored by a quadrupole mass spectrometer (M-201QA-TDM, Canon Anelva) for all the isotopic molecules of CO<sub>2</sub> (at *m/e* = 44, 46 and 48).

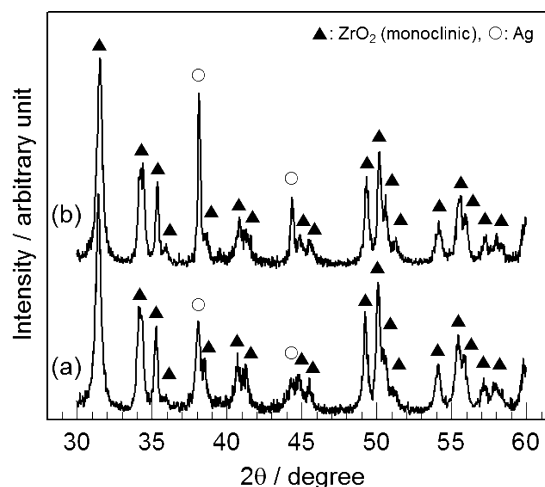


Fig. 1. XRD patterns of (a) Ag/ZrO<sub>2</sub>(NP) and (b) Ag/ZrO<sub>2</sub>(IMP).

Direct observation of Ag particles by TEM was performed with a JEM-2100 (JEOL) operating at an acceleration voltage of 200 kV. The crystal structure of the samples was identified by XRD (Rigaku MiniFlexII) measurements using Cu K $\alpha$  radiation at 30 kV and 15 mA. The XPS analyses were performed with a Kratos analytical ESCA-3400 (Shimadzu) using Mg K $\alpha$  radiation ( $h\nu = 1253.6$  eV). The binding energy was corrected by the contaminated carbon (284.6 eV).

Temperature-programmed reduction by CO (CO-TPR) was performed to investigate the reducibility of the catalysts. Prior to each experiment, the sample was pretreated in situ in a flow of 10% O<sub>2</sub>/He at 400 °C for 1 h and then cooled to room temperature. After purging with He, the TPR profiles were obtained from room temperature to 400 °C in a 30 cm<sup>3</sup> min<sup>-1</sup> flow of 0.5% CO/He at a heating rate of 10 °C min<sup>-1</sup>. The effluent gas was analyzed with an on-line quadrupole mass spectrometer (PFEFFER OminiStar).

The diffuse reflectance FT-IR spectra of adsorbed CO, as a probe molecule, were taken with a Nicolet 6700 FT-IR spectrometer at a resolution of 4 cm<sup>-1</sup>. Prior to each experiment, 30 mg of a sample placed in a diffuse reflectance high temperature cell (Spectra Tech) fitted with CaF<sub>2</sub> windows was pretreated in situ by heating at 400 °C in flowing 10% O<sub>2</sub>/He, and then cooled to 50 °C in flowing He. The background spectrum of the clean surface was measured for spectra collection. The reaction gas containing 0.5% CO and He as the balance gas was fed to the sample at a flow rate of 50 cm<sup>3</sup> min<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Crystal structure and morphology of Ag/ZrO<sub>2</sub>(NP) and Ag/ZrO<sub>2</sub>(IMP)

Fig. 1 shows XRD patterns of Ag/ZrO<sub>2</sub>(NP) and Ag/ZrO<sub>2</sub>(IMP). In addition to XRD peaks indexed to a monoclinic phase of ZrO<sub>2</sub>, distinct XRD peaks due to Ag(1 1 1) and Ag(2 0 0) were detected at 38.1 and 44.4°, respectively, for both Ag/ZrO<sub>2</sub> samples. The crystallite size of Ag in Ag/ZrO<sub>2</sub>(NP) (14.3 nm) was found to be smaller than that in Ag/ZrO<sub>2</sub>(IMP) (63.2 nm).

Fig. 2 shows TEM images of Ag/ZrO<sub>2</sub>(NP) and Ag/ZrO<sub>2</sub>(IMP). As seen in Fig. 2(b), hemispherically shaped Ag particles were found to be dispersed on ZrO<sub>2</sub> support with the size of ca. 5 nm for Ag/ZrO<sub>2</sub>(IMP). The particle size of Ag estimated by TEM is quite smaller than that by XRD. This is probably due to inhomogeneous dispersion of Ag particles in Ag/ZrO<sub>2</sub>(IMP). In fact, as given in Fig. 2(c), the presence of large Ag particles with the size of 200 nm was also observed. On the other hand, the presence of spherically

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