



Catalytic oxidation of carbon nanotubes with noble metal nanoparticles



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ABSTRACT

Catalytic oxidation of multi-walled carbon nanotubes (MWCNTs) with some noble metal nanoparticles was observed by environmental transmission electron microscopy (E-TEM). Amoeba-like movement of the nanoparticles was observed even at a temperature of $\sim 400^\circ\text{C}$, which is much lower than the melting points of any of the metals. In particular, rhodium particles reacted intensely with MWCNTs, and assumed a droplet-like shape. On the other hand, gold particles caused very little erosion of the MWCNTs under the conditions of this study.

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1. Introduction

Due to the thermal efficiency of diesel engines, increasing their use is considered a promising approach for the reduction of CO_2 emissions. However, the presence of particulate matter (PM) in diesel engine exhaust gas is a significant drawback of this approach. Installation of a catalyzed diesel particulate filter (CDPF) in the exhaust system can be an effective solution to this problem. A CDPF consists of a porous ceramic monolith and catalytic nanoparticles (NPs) such as platinum (Allansson et al., 2002; Edgar et al., 2000; Mogensen et al., 2009). The PM is first collected on a ceramic filter and is subsequently combusted with NPs. The catalytic NPs play an important role in the passive regeneration of the filter by enabling the oxidation of the diesel PM at the typical exhaust temperatures of $300\text{--}400^\circ\text{C}$ for an operating engine. In the absence of the catalyst, PM can be oxidized at appreciable rates only at temperatures over 600°C . In a diesel engine, such a high temperature can be achieved only under fully loaded conditions or through heating by an additional electric heater in a built-in diesel particulate active-reduction system. Thus, the development of a highly efficient combustion catalyst is directly connected with energy

conservation. In the case of noble metal-containing catalysts, reduction of the amount of catalyst required for combustion is also important. Therefore, quantitative methods for the evaluation of the catalytic properties of carbon soot combustion are desired. The reactivity of a soot-combusting catalyst depends on both its intrinsic properties and the degree of physical contact between the catalyst and the soot (van Setten et al., 2000; Matsuda et al., 2012). However, since it is difficult to control the degree of physical contact, estimation of their catalytic properties is challenging.

In the present study, the intrinsic catalytic properties of noble metal NPs were roughly estimated by observing combustion of multi-walled carbon nanotubes (MWCNTs) loaded with noble metal NPs without any supporting ceramics. While catalytic gasification and growth of MWCNT controlled by vapor content have been already reported (Feng et al., 2011), we focused on catalytic oxidation of MWCNT as a model of reaction on CDPFs. Physical contact of catalytic metal and MWCNT in this study corresponds to so-called tight contact.

2. Materials and methods

For *in situ* observations, we employed a reaction science high-voltage electron microscopy (JEOL Ltd., JEM-1000K RS, 1000 kV) (Tanaka et al., 2013) and environmental transmission electron microscopy (E-TEM; Hitachi High-Technologies, H9500, 300 kV) (Kishita et al., 2008; Yaguchi et al., 2012) possessing a differential pumping system together with a wire heating holder

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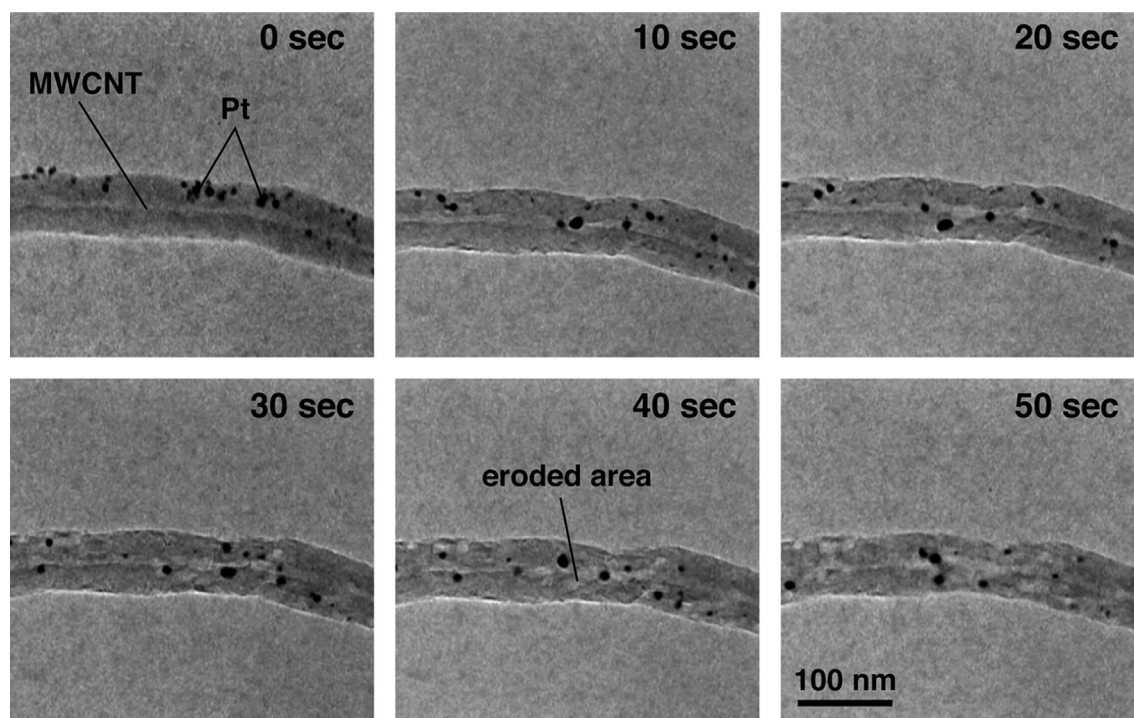


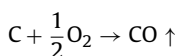
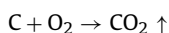
Fig. 1. TEM images of Pt on MWCNT extracted from a movie recorded by *in situ* observation with 300 kV E-TEM.

(Kamino et al., 2005a; Kamino and Saka, 1993). Samples were prepared by mixing commercially available metal nanocolloids (Pt, Au, Ir, Rh, and Pd; Wako Pure Chemical Industries, Ltd., particle sizes are 2–5 nm) and MWCNTs (Wako Pure Chemical Industries Ltd., or Sigma–Aldrich Co., LLC) in ethanol. Each sample was placed directly on a tungsten wire in the heating holder, heated to $\sim 400^\circ\text{C}$ under vacuum in the TEM column, and then exposed to oxygen gas at a pressure of ~ 2 Pa. TEM images were recorded using a charge-coupled device (CCD) camera as movie files.

3. Results and discussions

Fig. 1 shows a series of TEM images of erosion of a MWCNT by Pt NPs. These images were extracted from a movie recorded prior to the introduction of oxygen a few minutes later.

Although, some Pt NP agglomeration was observed due to heating, the sample was almost unchanged under vacuum. This small change with heating up to 400°C may be caused by deformations of surfactants included in colloidal solutions, while movement of gold NPs on MWCNT at 800°C had been reported (Kamino et al., 2005b). After exposure to oxygen gas, Pt NPs moved rapidly on the MWCNT surface and coalesced into large particles. It was also observed that Pt NPs assumed a droplet-like shape during their motion even at temperatures that were much lower than the melting point of 1768°C (see Supplementary movie 1). A fraction of the MWCNT was eroded during oxygen exposure of several tens of seconds. This erosion may be caused by either or both of the following catalytic oxidation reactions involving MWCNTs (Severin et al., 2009).



Since these oxidative reactions did not progress without any NPs even at 400°C , it is clear that Pt NPs possess catalytic activity.

As shown in the movie, the evolution of the erosion area tracks the movement of the NPs. This result shows that the above reactions proceeded only in the immediate neighborhood of the interface between the catalytic metal and the carbon. A suggested mechanism for the movement of metal particles on the MWCNTs is shown in Fig. 2.

Immediately after the introduction of oxygen, carbon atoms adjacent to metal NPs are combusted and released from the MWCNT surface. Metal NPs are then drawn closer to the edge formed by the MWCNT erosion. Movement of the NPs and MWCNT erosion are repeated due to continuous catalytic oxidation at the interface between the graphitic edge and the metal NPs. Fig. 3 shows TEM images of Pt NPs loaded on a very straight MWCNT (see also Supplementary movie 2).

In this case, the combustion reaction progressed preferentially along the graphitic layers. This implies that the combustion rate at defects such as graphitic edges is higher than that within the graphitic layer. This difference may be caused by the high reactivity of dangling bonds or functional groups present at the edges. On the other hand, no preferential erosion direction within the plane of the graphitic layer was found in this study, in contrast to previous reports on the catalytic hydrogenation of graphene (Schäffel et al., 2009; Melinte et al., 2014; Ma et al., 2014).

Droplet-like behavior and movement following erosion were also found for Ir, Pd, Rh, and Au NPs (see Supplementary movies 3–6). However, the combustion rate for catalysis with Au NPs was quite low compared with that of the other noble metals. At the other

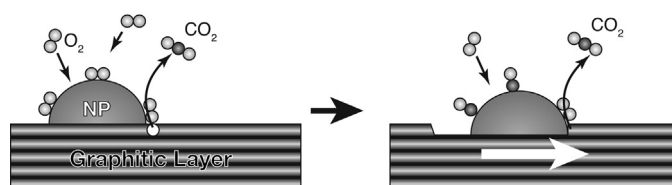


Fig. 2. Schematic model of catalytic nanoparticle motion.

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