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Ozone-assisted catalysis of CO: *In situ* Fourier transform IR evidence of the cooperative effect of a bimetallic Ag-Pd catalyst

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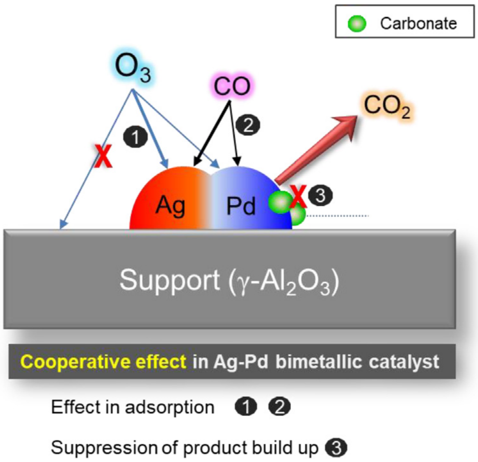
HIGHLIGHTS

- Ozone-assisted catalysis was able to remove CO efficiently at room temperature.
- Bimetallic Ag-Pd catalyst exhibited a cooperative effect.
- *In situ* FTIR measurement provided useful insights into the mechanism of the catalytic reaction.

GRAPHICAL ABSTRACT



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ABSTRACT

The room-temperature oxidation of CO using ozone-assisted catalysis (OAC) over monometallic or bimetallic catalysts supported on γ-Al_2O_3 is presented. Within the tested particle size range, ozone decomposition was insensitive to the size of the Ag particles (6.6–11.9 nm) at weight hourly space velocities of up to 360 $L{\cdot}g^{-1}{\cdot}h^{-1}$. Among the tested monometallic catalysts (Ag Pd, Fe, Mn, and Cu), Ag showed the highest activity for CO oxidation. Bimetallic catalysts (Ag-M or Pd-M where M = Cu, La, Ru, and Fe) were also considered by adding a second metal or perovskite oxide ($LaFeO_3$) to Ag. A cooperative effect was observed with the bimetallic Ag-Pd catalyst for the OAC of CO oxidation at room temperature, whereas the other bimetallic catalysts showed slightly lower performance compared to the monometallic catalyst. A high ozone utilization efficiency of 0.94 was achieved with the bimetallic Ag-Pd/γ-Al_2O_3 catalyst. High-angle annular dark-field scanning tunneling electron microscopy (HAADF) and energy dispersive X-ray (EDX) spectroscopy measurements confirmed the proximity of the two components, which is essential for their interaction. The *in situ* FTIR measurements revealed that the cooperative effect in the bimetallic Ag-Pd catalyst involved modification of CO adsorption and the suppression of product accumulation. Two typical IR absorption bands of linear- (2090 cm^{-1}) and bridge-CO (1918 cm^{-1}) on Pd disappeared in the presence of Ag nanoparticles. Thus, the presence of Ag in contact with Pd inhibited the

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accumulation of carbonates, which led to enhanced catalytic performance. Adsorption site-dependent CO oxidation on Pd was also confirmed by the *in situ* Fourier transform IR measurement.

1. Introduction

Carbon monoxide (CO) is a well-known toxic gas, and it has been received a considerable attention in the field of catalyst studies. Effective CO removal is still important in diverse fields such as indoor air treatment, vehicle emissions [1], and fuel cells [2]. The catalytic removal of CO has long been the subject of intense study. The catalytic performance depends on the type of active materials, support, and their combination. Gold (Au) is known to possesses extremely high catalytic activity for CO oxidation, even at temperatures as low as −70 °C [3]. However, the catalytic activity of Au easily disappears when it is exposed to hydrocarbons [4]. Transition metal-supported catalysts other than Au catalyst usually requires mild heating, for example, between 50 °C and 100 °C.

Nonthermal plasma is characterized by the action of reactive radicals, which oxidize various volatile organic compounds (VOC), NO, and CO. However, the reaction rate coefficients of the major oxidizing species are not high enough to ensure the complete CO removal by the plasma process alone. The most powerful oxidizer, OH radical, has reaction rate coefficient of $1.4 \times 10^{-13}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$ at 298 K. Ozone and its derivative, O(^{3}P), have even slower rate coefficients of $1.4 \times 10^{-17}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$ and $4 \times 10^{-25}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$, respectively. This intrinsic limitation has led researchers to consider a hybrid plasma catalysis system in the form of a single-stage or two-stage process [5]. Ozone-assisted catalysis (OAC) is one type of two-stage plasma catalysis. In contrast to the other type of two-stage processes, where the gas mixture for treatment passes through a plasma reactor, only air or pure O_2 is fed to the plasma reactor to generate O_3. The O_2-fed ozonizer, in turn, provides an important advantage of complete control over NOx formation, even at a high power input to the plasma reactors [6]. The injection of O_3 lowers the temperature window of the catalyst to a far lower range than that in air without ozone [7]. Although many studies have been conducted on the OAC of benzene [8,9], toluene [6,10–12], isopropyl alcohol [13], and VOC mixtures [14,15], there have been relatively few studies performed to screen effective catalysts for CO control [13,16,17]. One of the early attempts for CO removal by OAC dates back to 1921 [18], where two-stage dielectric barrier discharge (DBD) and various catalysts were compared, and a Ag asbestos catalyst was found to be the most effective. Another important issue is that platinum group metals (PGM; Pt, Pd, and Rh) are not essential elements in OAC. The most widely studied compounds for OAC are manganese oxides (MnO*x*), which are cheap and abundant, but MnO*x* compounds have low catalytic activity for CO oxidation. In summary, only a limited number of catalysts have been tested for OAC, and more must be investigated.

In this study, we focused on the screening of various metals (M) supported on γ-Al_2O_3, either in the form of monometallic or bimetallic catalysts. Bimetallic catalysts for the thermal catalysis of CO have been studied over Ag-Au/TiO_2 [19], Pt-Pd/γ-Al_2O_3 [20], Ag-Pd/pumice [21], and Mn/Ag composites [22]. To date, there have been no reports of the OAC of CO over bimetallic catalysts. X-ray diffractometry (XRD), high angle annular dark field scanning tunneling electron microscopy (HAADF-STEM) images and energy-dispersive X-ray spectroscopy (EDS) mapping were used for the characterization of the catalysts. *In situ* Fourier transform infrared (FTIR) spectra were collected to unravel the cooperative effect observed with the bimetallic Ag-Pd catalysts.

2. Experimental

2.1. Experimental setup

The experimental setup is schematically illustrated in Fig. 1. Ozone was generated using the oxygen-fed dielectric barrier discharge (DBD) reactor. The DBD reactor was made of a cylindrical quartz tube with a 1.5 mm gap and a 20 cm effective length. An AC neon transformer with a commercial frequency (50 Hz) was used. Ozone-assisted catalysis was performed at room temperature. Unless otherwise noted, throughout in this study, the amount of catalyst was 50 mg throughout in this study. A K-type thermocouple placed downstream of the catalyst bed to measure the temperature increase during the reaction. The total gas flow rate was constant at 300 mL min^{-1}. Each gas was controlled using a mass flow controller (Kofloc Co., FCC-3000). The CO and CO_2 concentrations were measured using an FTIR (Perkin Elmer SpectrumOne) spectrometer equipped with a long-path gas cell (6.4 m path length) and a

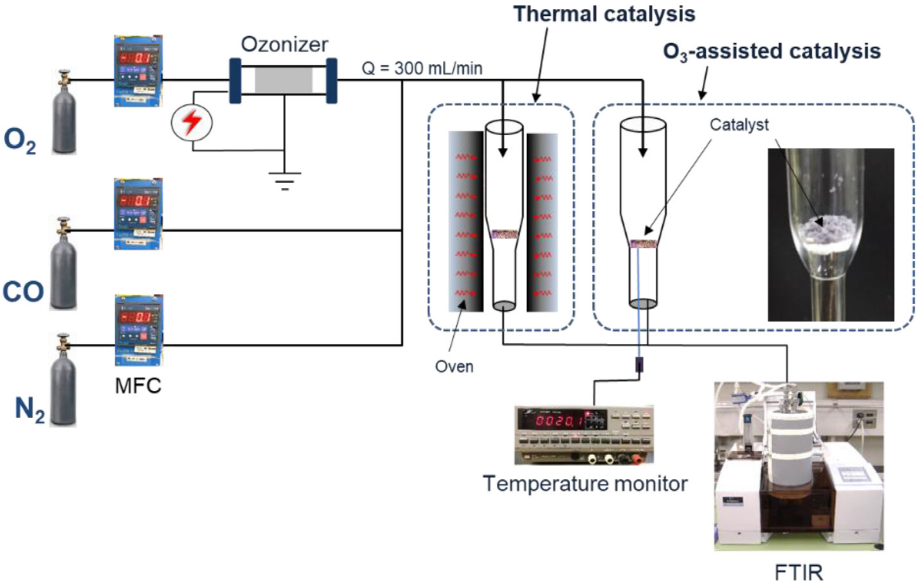

Fig. 1. Experimental setup.