Direct loading of fine particles of Pd on activated carbon from acidic aqueous solution and its NO conversion ability

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Direct loading of fine particles of metallic Pd on an activated carbon was found in an acidic solution of PdCl₂ at room temperature. Pd-loaded activated carbons thus prepared showed almost 100% conversion of NO at a temperature above 350°C. The amount of Pd loaded on activated carbon could be controlled by the concentration of PdCl₂ in the solution.

KEYWORDS: Activated carbon, Palladium metal, NO conversion

1. Introduction

Nitrogen oxides (NOₓ, x = 1, 2) are exhausted not only from mobile sources, such as automobile, ship and airplane, but also from stationary ones, such as boiler and incinerator at high temperature combustion. NOₓ gases are one of the reasons for atmosphere pollution and are supposed to cause acid rain and photochemical smog. Therefore, various methods and processes have been proposed and applied to decrease the NO concentration in air, although still many fundamental and applied researches are going on. The reduction of NOₓ by using some catalysts is one of the promising methods.

For catalytic NO conversion, various metals were reported to be effective catalysts and different substrates have been employed to keep highly dispersed metal particles1)-11). It has been reported that carbon substrates have the advantage that reducing agents, such as ammonia, carbon monoxide and hydrocarbon, are not necessary to be added into the reaction system because the substrate carbon acts as a reducing agent9). Different processes have been applied to load fine particles of different metals onto activated carbons8). Among these processes, the solutions containing metal ions have frequently been used as a source of metals because of simple procedure and economy in energy. However, the deposition of metal compounds, such as metal halides and hydroxides, usually occurs and further heat treatment at high temperatures is needed in order to get metal particles. The high temperature treatment of metal compounds deposited has a possibility to exhaust corrosive halogen gases and also to agglomerate reduced metal particles, which are not desirable in order to get a high performance of these catalysts.

In the present work, fine particles of metallic Pd were found to be loaded on the surface of activated carbon by a simple immersion into an acidic aqueous solution of PdCl₂ at room temperature. For these Pd-loaded activated carbons, NO conversion ability was examined.

2. Experimental

Commercially available activated carbon (AC) produced from coconut shells was used as the substrate, of which the BET surface area was about 1000 m²/g and the grain size was about 0.3 mm.

The AC of 1.0 g was dispersed in 300 mL solution of palladium (II) chloride PdCl₂ with different concentrations (1.2 - 4.8 × 10⁻³ mol/L) for 1 h, filtered under reduced pressure for 5 min and then dried at 105°C for 12 h. In order to get relatively high concentration of PdCl₂ aqueous solution, HCℓ had to be added into the solution.

The samples thus prepared were characterized by X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The amount of Pd mounted was determined by burning-off the substrate AC at 1100°C in air using TG apparatus. Pd metals loaded on AC was once oxidized on the course of heating in air, but reduced to metal again above 900°C.

The NO conversion by Pd-loaded AC samples was examined by the following procedure. The Pd-loaded AC of 0.05 g was heated in between lumps of glass wool in a glass tube (inner diameter of ca. 4 mm) at 500°C for 1 h in a flow of high-purity He (a flow rate of
100 mL/min) in an electric furnace, and then the He-diluted NO gas (NO concentration of ca. 1000 ppm) was introduced with a flow rate of 100 mL/min (space velocity of 6000 h⁻¹) to the sample glass tube. The temperature of the sample decreased in steps of every 50°C from 500 to 250°C, for each temperature step being kept for 1 h. At each temperature NO concentration of the effluent gas was determined using a NOx analyzer. NO conversion ratio by the sample was defined by the relative percentage of the decrease in NO concentration in effluent gas to the initial NO concentration.

3. Results and Discussion

3.1 Palladium deposition onto activated carbon

No deposition of either metallic Pd or Pd compounds on AC was detected from the alkaline solutions of PdCl₂. However, metallic Pd deposition was detected under acidic conditions without heat treatment, as shown in Fig. 1a. XPS spectra for the samples prepared showed the presence of Pd metal, as shown on 3.5 mass% Pd-loaded sample in Fig. 1b.

On XRD pattern, only Pd metal was detected, as shown in Fig. 1a. Pd (II), in addition to Cl, was observed together with Pd metal on XPS spectra, as shown in Fig. 1b. Since XPS gave only the information on the surface, these observations suggest that some amount of PdCl₂ remained possibly on the surface of Pd metal particles under the present condition for the separation of the activated carbon particles from PdCl₂ solution, but the principal deposited species were metallic Pd. The binding energy for the 3d₅/₂ state of Pd metal was a little higher than the reported value (335.1 eV), which was supposed to be due to the interaction with the substrate carbon, i.e., a little less electron density on Pd metal particles.

In Table 1, the amount of Pd loaded is shown on the samples prepared, together with the concentrations of PdCl₂ and HCl in aqueous solutions used. The result shows that the amount of Pd loaded increases with increasing PdCl₂ concentration. When the amount of Pd loaded was plotted against the concentration of PdCl₂ in the solution, almost linear relation was obtained, except that the sample prepared in the highest concentration of PdCl₂ gave a little lower value than expected, which may suggest that loading of about 11 mass % Pd is close to the limit for the present process.
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In Fig. 2, a transmission electron micrograph is shown on the sample loaded 3.5 mass % Pd, where many round particles with the sizes of less than 10 nm are observed. Since these particles have dark contrast, these are reasonably supposed to be Pd metals. These Pd particles are always observed on the substrate carbon which has light contrast.

In the present work, fine particles of metallic Pd could be successfully loaded on the surface of activated carbon directly, any heat treatment being not necessary. It was confirmed that the presence of activated carbon was essential in order to get the direct deposition of metallic Pd particles. When an acidic aqueous solution of PdCl₂ with HCl was dried up, only PdCl₂ was obtained. When porous γ-Al₂O₃ was also immersed into PdCl₂ solution, instead of activated carbon, no Pd was loaded on γ-Al₂O₃. Also porous anatase-type TiO₂, which has a high surface area as 300 m²/g and been used for photocatalyst samples in a series of our experiments on carbon-coated anatasel², ¹³, was used, but no Pd deposition was detected.

3.2 Performance for NO reduction

In Fig. 3, NO conversion is plotted against the amount of Pd loaded on the samples as a function of reaction temperature. At low temperature as 250°C, the reduction of NO does not proceed markedly. By the increase of reaction temperature above 300°C, NO conversion increases markedly and above 350°C almost 100 % NO could be converted to the reduced phases.

In Fig. 4, changes in gas concentration in the effluent gas with reaction temperature are shown on 3.5 mass % Pd-loaded sample. At 250°C, NO conversion is very low, but at 300°C only small amount of NO (about few ppm) was detected and above 350°C no NO (100 % conversion of NO), as shown in Fig. 3. At the reaction temperature of 300 ～ 400°C, the reduction of NO was not complete, still certain amount of N₂O was observed, together with N₂. Above 450°C, only N₂ was detected, no N₂O, revealing the complete reduction of NO to N₂. At all reaction temperatures, CO₂ was observed, proving that the substrate activated carbon worked as reducing agent. No CO formation was detected.

NO conversion efficiency does not depend on the amount of Pd loaded, except one experimental point at 300°C for 7.6 mass % Pd loaded. This sample shows much lower NO conversion at 300°C in comparison with the samples with lower and higher Pd loading, and also slightly lower at 350°C. However, this sample showed 100 % conversion of NO above 400°C. Even the sample loaded with as small as 3.5 mass % Pd shows high NO conversion efficiency, comparable to the samples loaded with higher amounts. This high efficiency in NO conversion is supposed to be due to small sizes of Pd particles, which is easily obtained in the present process because of no heat treatment at high temperatures.

The low efficiency observed on the sample with 7.6 mass % Pd might be due to the agglomeration of Pd particles, even though it was not observed under TEM observation. This agglomeration is reasonably supposed to give more marked effect at a lower reaction temperature, markedly observed at 300°C than above 350°C in the present work. The possibility of this agglomeration of Pd particles seems to be the higher in the larger amount of Pd loaded. A low efficiency of NO conversion was observed below 350°C, when another sample with about 9 mass % Pd was prepared, in which large Pd particles were detected under TEM.

4. Concluding Remarks

Fine metallic Pd particles of less than 10 nm in size were successfully loaded on a commercially available activated carbon from acidic aqueous solutions of PdCl₂ at room temperature. The amount of Pd loaded was able to be changed by controlling the concentration of PdCl₂ in the solution. Even the smallest loading of 3.5 mass % Pd, however, could give 100 % conversion of NO gas at a temperature above 350°C. This loading process has some
advantages: a high efficiency of Pd catalysts for NO conversion and no necessity to be heat-treated at high temperatures in order to get Pd metal, in addition to the merit of no necessity of reducing gas, which is common to the carbon-Pd systems.

Maximum loading of total amount of Pd was estimated to be 11 mass% to the substrate activated carbons. On the basis of the present work, however, the low amount of loading of Pd, lower than 6 mass%, was recommended in order to get high dispersion of fine Pd particles on the surface of activated carbon, from which high efficiency of NO conversion was obtained.

The success of this direct loading onto activated carbons was supposed to be due to the use of acidic aqueous solutions of PdCl₂. However, the detailed mechanism was not clearly understood. It might be important to study the role of functional groups on activated carbon surface for Pd loading.

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References