$AlPO_4$ as a Support Capable of Minimizing Threshold Loading of Rh in Automotive Catalysts

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A recent serious problem with precious metals is concerned with their rapidly increasing use as catalysts in automobile exhaust after-treatment. The most extreme example is found in Rh; its use in so-called the three-way catalysis for gasoline engines has increased more than 30% over the past 5 years to being currently more than 85% of the total demand.[1] Rhodium is among the scarcest of precious metals and is critical to the removal of noxious nitrogen oxides (NO_x), having mainly no viable substitutes.[2−5] Upon exposure to a high-temperature exhaust, nanoparticles of precious metals in the catalytic converter are agglomerated into large grains with low specific surface areas and hence low catalytic activities. To counter this effect, conventional automotive catalysts are loaded with an excess amount of precious metals, ensuring that the performance meets the present emission standards. To lessen the amount of precious metals in automotive catalysts, a new concept of supported Pd catalyst that achieves self-regeneration has been recently proposed,[6] but the design concept effective in minimizing the loading of most expensive Rh has not yet been developed. Here we show that aluminum phosphate ($AlPO_4$) becomes an efficient and robust support material to produce optimum metal−support interactions that can reduce significantly Rh loading, owing to thermally stable and highly dispersed Rh nanoparticles anchored strongly onto the phosphate surface.

For the preparation of $AlPO_4$, a solution of 0.05 mol of H_3PO_4 in 50 mL of deionized water was added dropwise to a solution containing 0.05 mol of $Al(NO_3)_3$ in 50 mL of deionized water with vigorous stirring. Then, an aqueous ammonia solution (25%) was added dropwise until the pH of the supernatant was 4.5. The white gel thus obtained was washed with deionized water, dried in air at 100 °C, and calcined in air at 1000 °C for 5 h (BET surface area: 82 $m^2\ g^{-1}$). Rh loaded on $AlPO_4$ with different loadings (0.001−0.4 wt % as Rh metal) was prepared by impregnation of an aqueous solution of $Rh(NO_3)_3$, followed by drying (100 °C) and air calcination (600 °C, 3 h). Rh catalyst supported on 3 wt % La_2O_3 added γ-Al_2O_3 (134 $m^2\ g^{-1}$) was also prepared in a similar way as a reference. The addition of La is known to suppress the surface area loss due to the phase transformation from γ-Al_2O_3 to α-Al_2O_3.[7,8] Our catalytic test was carried out after aging catalysts in a stream of water vapor (10% H_2O/air, 900 °C). The catalyst (50 mg) was heated from room temperature to 600 °C at constant rate of 10 °C•min^{-1} with supplying a simulated exhaust gas mixture containing NO (0.050%), CO (0.510%), C_3H_6 (0.039%), O_2 (0.400%), and He (balance) supplied at 100 cm^3•min^{-1} (space velocity of about 100 000 h^{-1}).

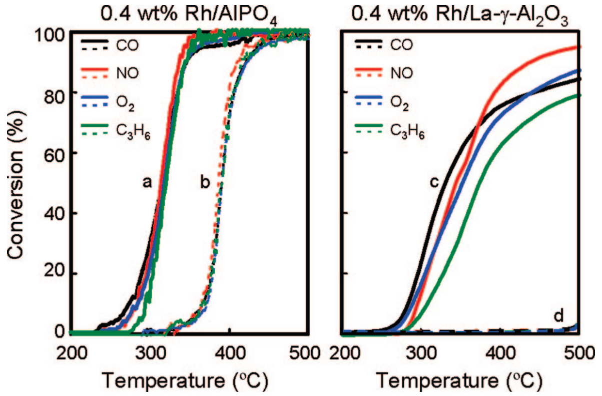

Figure 1. Catalytic light-off of a stream of NO, CO, C_3H_6, and O_2 over supported Rh catalysts. a, 0.4 wt % Rh/$AlPO_4$ (25 h). b, 0.4 wt % Rh/$AlPO_4$ (500 h). c, 0.4 wt % Rh/La-γ-Al_2O_3 (25 h). d, 0.4 wt % Rh/La-γ-Al_2O_3 (500 h). The times in parentheses are for thermal aging in a stream of 10% H_2O/air at 900 °C before the catalytic test. The catalyst (0.05 g) was heated at the constant rate of 10 °C•min^{-1} in a stream of gaseous mixture of NO (0.050%), CO (0.510%), C_3H_6 (0.039%), O_2 (0.400%), and He (balance) supplied at 100 cm^3•min^{-1}.

Figure 1 exhibits the temperature dependences of conversion efficiencies of NO, CO, C_3H_6, and O_2 in a simulated exhaust with a stoichiometric air-to-fuel ratio. The both catalysts after 25 h-aging initiated the reaction at around 250 °C. However, 0.4 wt % Rh/$AlPO_4$ (a) achieved 90% conversion at about 350 °C, compared to more than 500 °C required for 0.4 wt % Rh/La-γ-Al_2O_3 (c). The steep rise of conversion efficiencies within a narrow temperature range is one advanced characteristic common to Rh/$AlPO_4$ catalysts with lower Rh loadings down to 0.01 wt %. A more drastic difference was observed after aging at 900 °C for 500 h; the activity of the Rh/La-γ-Al_2O_3 (d) was totally lost, whereas Rh/$AlPO_4$ (b) preserved the light-off characteristic, which

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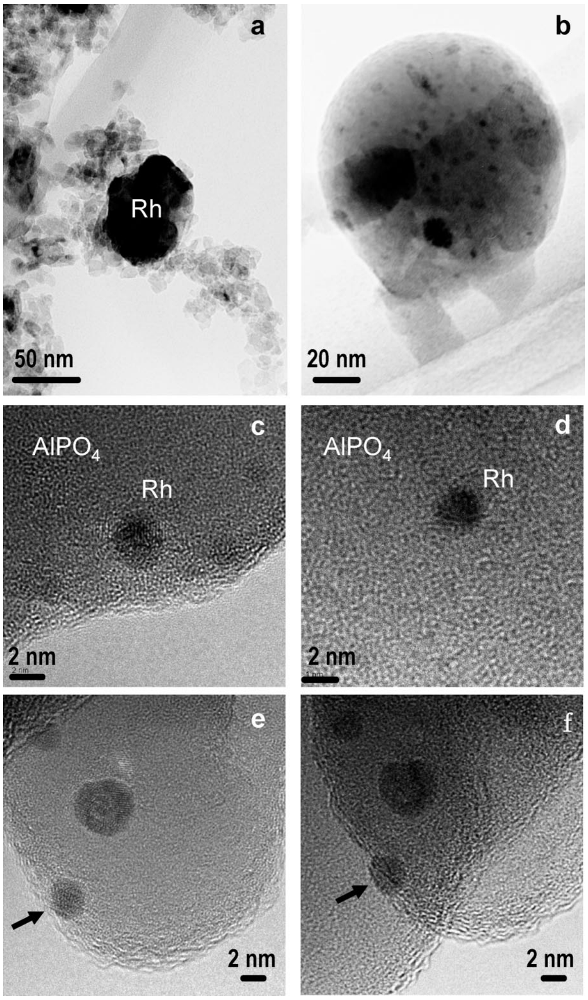

Figure 2. TEM images of supported Rh catalysts. a, 0.4 wt % Rh/La-γ-Al_2O_3 aged in a stream of 10% H_2O/air at 900 °C for 500 h; b, 0.4 wt % Rh/$AlPO_4$ aged in a stream of 10% H_2O/air at 900 °C for 500 h; c, as-prepared 0.4 wt % Rh/$AlPO_4$; d, 0.4 wt % Rh/$AlPO_4$ aged in a stream of 10% H_2O/air at 900 °C for 500 h; e and f, as-prepared Rh/$AlPO_4$ taken from different angles of an incident beam (±15°).

proves a high thermal stability. The Rh/$AlPO_4$ catalyst is found to be the most active among the Rh catalysts supported on conventional metal oxide supports (Supporting Information).

To investigate the reason for the different catalytic activity between Rh/$AlPO_4$ and Rh/La-γ-Al_2O_3 after the long-term aging, the local structure of Rh on each support material was examined using TEM observation. Figure 2a,b shows representative images of 0.4 wt % Rh loaded on La-γ-Al_2O_3 and $AlPO_4$, respectively, after aging in a stream of 10% H_2O/air at 900 °C for 500 h. Clearly, Rh loaded on La-γ-Al_2O_3 is isolated from the support and agglomerated substantially to form grains larger than 50 nm, which correlate with a low catalytic performance (Figure 1d). The aging of 500 h decreased the BET surface areas from 121 $m^2\ g^{-1}$ to 54 $m^2\ g^{-1}$ (Rh/La-γ-Al_2O_3) and from 63 $m^2\ g^{-1}$ to 26 $m^2\ g^{-1}$ (Rh/$AlPO_4$). The phase transformation from γ- to α-Al_2O_3 was not detected by XRD and electron diffraction. Thus, observed deactivation of Rh/La-γ-Al_2O_3 is thus more than expected from the surface area loss and should be associated with the high mobility of Rh species on the Al_2O_3 surface. Thermal deactivation of Rh/La-γ-Al_2O_3 has frequently been pointed out,[9,10] when the aging is carried out even at medium temperature, ≥600 °C, in the presence of O_2. A number of explanations have been proposed for thermal deactivation of Rh/La-γ-Al_2O_3 including dissolution of Rh oxide into Al_2O_3, formation of Rh aluminate ($RhAlO_x$), encapsulation of Rh by Al_2O_3, and other strong interactions.[9−14] But, high-temperature aging of the present study caused more serious deterioration on the catalyst structure and catalyst performance as shown in Figure 1d.

In contrast to Rh/La-γ-Al_2O_3, a TEM image from Rh/$AlPO_4$ (Figure 2b) confirms that highly dispersed Rh particles of diameters around 1−4 nm mostly remain, although a small number of agglomerates more than 10 nm are also present. Particle growth of Rh is therefore suppressed to a significant extent on the surface of $AlPO_4$. Such thermostable Rh nanoparticles are presumably responsible for the preserved light-off characteristics in the catalytic test (Figure 1b). High-resolution images in Figure 2c,d were taken from 0.4 wt % Rh/$AlPO_4$ as calcined at 600 °C and after subsequent aging in a stream of 10% H_2O/air at 900 °C for 500 h, respectively. As prepared catalyst shows that Rh particles with diameter of 1−4 nm are highly dispersed on a low-crystalline $AlPO_4$. This is consistent with the mean Rh particle size, 2.8 nm, which is estimated from metal dispersion (40%) determined by CO chemisorption at 50 °C (Supporting Information). It should be noted that Rh nanoparticles were preserved even after the aging for 500 h (Figure 2d), but such nanoparticles could not be found in the aged Rh/La-γ-Al_2O_3. The metal dispersion measurement (Supporting Information) supports that this conclusion is statistically correct. Figure 2e,f shows high-resolution images taken from the same position but different angles of the incident beam to study the morphology of Rh nanoparticles. Judging from comparison of a Rh nanoparticle shown by an arrow, it looks like a plate spreading over the $AlPO_4$ surface rather than a hemisphere. This type of morphology proves the strong interaction with the $AlPO_4$ surface, which anchors Rh nanoparticles to be stabilized against coalescence even during high-temperature aging.

Recently, several researchers have reported the dynamic structural change of the Rh nanoparticles in automotive catalysis.[15−17] Growth and disruption of Rh clusters occur depending on gas species (CO, NO, O_2, and others) and reduction/oxidation atmosphere. However, it is difficult to prevent the sintering of Rh species in the presence of excess O_2 and water vapor at such high temperatures (≥900 °C).

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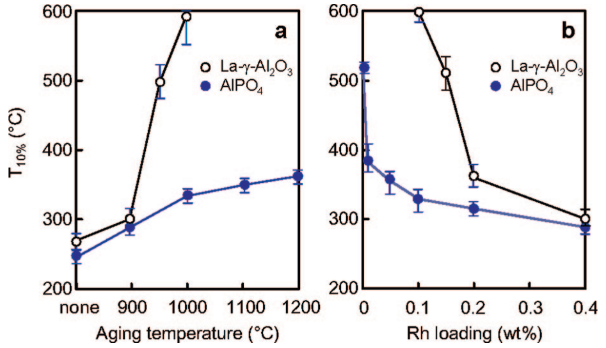

Figure 3. Light-off temperature ($T_{10\%}$) of NO conversion. Light-off is defined as 10% conversion of NO. a, Dependence on temperature where the catalyst was aged in a stream of 10% H_2O/air for 25 h (0.4 wt % Rh). b, Dependence on the amount of Rh loading (aged in a stream of 10% H_2O/air at 900 °C for 25 h). Error bars correspond to the maximum and minimum values in two or three runs of the catalytic reaction. The catalyst (0.05 g) was heated at the constant rate of 10 $°C \cdot min^{-1}$ in a stream of gaseous mixture of NO (0.050%), CO (0.510%), C_3H_6 (0.039%), O_2 (0.400%), and He (balance) supplied at 100 $cm^3 \cdot min^{-1}$.

XPS measurement of the present system has demonstrated that a large part of the Rh surface was in the form of oxide before and after the aging in air. Unlike the Al_2O_3 case, however, Rh oxide did not cause solid-state reactions with $AlPO_4$. Nonreactive but strong anchoring effect can be considered to be a reason for the thermal stability of highly dispersed Rh nanoparticles. More detailed analysis of the metal−support interaction by means of EXAFS is now under investigation.

Because the critical measure of Rh catalysts is their ability to achieve the efficient NO reduction to N_2, the light-off of NO conversion in the simulated exhaust gas stream was used as an indicator of catalytic activity. Figure 3a plots the light-off temperature, $T_{10\%}$, at which the NO conversion reaches 10%, for 0.4 wt % Rh-loaded La-γ-Al_2O_3 and $AlPO_4$ catalysts versus temperatures for 25 h of aging in a stream of H_2O/air. Rh/La-γ-Al_2O_3 underwent a strong deactivation by the aging at ≥1000 °C, where rapid growth of the Rh particle lost the active surface sites. By contrast, Rh/$AlPO_4$ could preserve its high catalytic activity up to 1200 °C. Such a high thermal stability demonstrates the potential durability in a real automotive catalytic converter. Figure 3b plots the $T_{10\%}$ as a function of the Rh loading on La-γ-Al_2O_3 and $AlPO_4$. The two Rh catalysts are almost comparable at the high loading of 0.4 wt %. In the case of Rh/La-γ-Al_2O_3, decreasing the Rh loading below a threshold value of 0.2 wt % deteriorated the catalytic activity, resulting in a steep rise of $T_{10\%}$. However, Rh/$AlPO_4$ retained much lower $T_{10\%}$ even at ≤0.2 wt %, and the threshold loading can be reduced down to 0.01 wt %. This corresponds to about 1/20 of the threshold Rh loading observed for Rh/La-γ-Al_2O_3. Although several conventional support oxides such as MgO, Al_2O_3, SiO_2, TiO_2, ZrO_2, and CeO_2 were also evaluated, $AlPO_4$ was found to be able to mostly minimize the threshold loading of Rh (Supporting Information).

Rh/$AlPO_4$ catalyst is not only capable of minimizing threshold loading of Rh but also expected to show the robustness required for a state-of-the-art automotive catalyst system. The phosphate surface should be effective in suppressing the catalyst deactivation caused by the adsorption of sulfur oxides (SO_x) and phosphate species. The thermal stability of our catalyst especially in an oxidizing atmosphere is most promising, because gasoline engine technology are directed toward lean-burn operations, which can reduce fuel consumptions and thus CO_2 emissions. The combination of low-temperature catalytic activity, high-temperature thermal stability, and tolerance to poisoning of our catalyst with minimum threshold loading of Rh may have broad significance for the practical high-temperature applications in the area of environmental protection.

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Supporting Information Available: Details on the comparison with conventional support materials and metal dispersion (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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