Pt Catalyst over SiO2 and Al2O3 Supports Synthesized by Aerosol Method for HC-SCR DeNOx Application

Riyan Zahaf1, Jae Wook Jung1, Zachary Coker2, Songkil Kim3, Tae-Youl Choi2, Donggeun Lee1*

1 School of Mechanical Engineering, Pusan Clean Coal Center, Pusan National University, Busan 609-735, Korea
2 Department of Mechanical and Energy Engineering, University of North Texas, Denton, TX 76207, USA
3 School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

ABSTRACT

Silica-supported platinum (Pt/SiO2) and alumina-supported platinum (Pt/Al2O3) catalysts have been prepared by an aerosol spray pyrolysis method. Systematic characterization of each catalyst using TEM, XRD, and XPS revealed that crystalline and metallic Pt nanoparticles were well dispersed on the surface of silica and alumina supports. The sintering effect on Pt particles over Al2O3 at high temperature (~250°C) is more prominent than those over SiO2; this suggests that there is stronger interaction between Pt particles and SiO2 support, when compared to Pt over Al2O3 support, resulting in Pt particles size below 3 nm. Moreover, steady-state catalytic experiments for selective reduction of nitrogen monoxide by propene have demonstrated that NOx conversions to N2O and N2 in Pt/SiO2 and Pt/Al2O3 catalysts are 29.8% and 55.8% at 250°C, respectively.

Keywords: Pt/SiO2; Pt/Al2O3; Aerosol; DeNOx Catalyst.

INTRODUCTION

Emission of NOx gases from both mobile and stationary sources causes serious environmental problems such as acid rain and photochemical smog (Pitchon and Fritz, 1999; Zhang et al., 2011; Wang et al., 2012). Thus, NOx treatment technologies have drawn much attention in view of catalysis, especially for treating various exhaust gases produced by state-of-the-art automobile engines (Haj et al., 2002). Hydrocarbon (HC) species are often emitted from automobiles under lean-burn operating conditions, in the forms of fragments (propane, propene, etc.) and/or more primitive polycyclic aromatic hydrocarbons (PAHs) which are known as mutagenic and carcinogenic compounds causing cataracts, kidney, and liver damage (Lu et al., 2011; Dong and Lee, 2009). Therefore, the European Union implemented increasingly stringent regulations on emissions, limiting HC and NOx concentrations to lower than 0.17 g km⁻¹ for passenger cars using diesel engines (The European Parliament and The Council of The European Union 2007).

The unburned HCs existing in the exhaust line can be used as a reducing agent for NOx treatment (Pitchon and Fritz, 1999; Haj et al., 2002) prior to tail-pipe emission, which is known as hydrocarbon-enhanced selective catalytic reduction (HC-SCR) of NOx. Using the HCs for NOx treatment enables more efficient fuel uses, while reducing HC and NOx emissions under lean-burn conditions (Burch, 2004; Wang et al., 2011). In this prospect, developing various catalysts for HC-SCR has been an intensive research area, which was initiated by Iwamoto et al. in 1990 (Iwamoto, 1990; Jayat et al., 1999). Then, Burch (Burch and Millington, 1995; Burch and Millington, 1996; Burch and Watling, 1997; Burch and Watling, 1998; Burch et al., 2002; Burch, 2004) performed a series of pioneering investigations for revealing catalytic performance and reaction kinetics of HC-SCR catalysts. Among various formulations of catalysts including Ag, Pd, Co, Ni, Au, Rh, and Cu, Pt-based catalysts showed excellent performance for NOx reduction at relatively low temperatures (Burch and Millington, 1995, 1996; Burch and Watling, 1997; Jayat et al., 1999; Burch et al., 2002). However, platinum suffers from three serious drawbacks: a narrow temperature window of operation, an objectionably high selectivity toward N2O (Burch and Watling, 1997) rather than a major species of NO or NO2, and a poor thermal stability (Asoro et al., 2010). In an attempt to resolve the issue of thermal stability, namely that Pt particles are easily sintered into large sizes, thereby significantly changing their behavior and catalytic performance (Suzuki et al., 2010), supporting materials such as silica and alumina have been introduced (Gonzalez et al., 1997; Nagai et al., 2006). As an example, Burch et al. (1996) reported that the maximum conversion of NO for Pt/SiO2 and Pt/Al2O3
catalysts reached 75% and 60%, respectively. Furthermore, such metal oxide supports are known to lower the working temperatures of Pt catalysts and minimize the undesirable corrosion effect of water vapor and sulfur oxides (SOx) (Burch and Watling, 1997; Gonzalez et al., 1997; Männikkö et al., 2012).

Recent studies suggested that specific catalytic activities are sensitive to not only the reducing gases and supporting materials, but also the dispersion, size, crystallographic nature, and microstructure of the Pt catalysts (Seker and Gulari, 2000; García-Cortés et al., 2003; Vaccaro et al., 2003; Després et al., 2004; Radic et al., 2004; Mulla et al., 2006). Given a limited amount of precious Pt in a sample, well-dispersed Pt particles with a moderate size (3–7 nm) are ideal for the efficient conversion of NOx (Jayat et al., 1999; Vaccaro et al., 2003; García-Cortés et al., 2003; Després et al., 2004). The existence of very large particles (> 10 nm) can cause a significant deterioration in particle dispersion, and can lead to less catalytic activity. Very small particles (< 2 nm) result in far better dispersion, but easy oxidation, which causes deactivation of the catalytic function (García-Cortés et al., 2003). In addition, crystallographic orientation of Pt determined by the ratio of Pt (100) peak to Pt (111) peak from X-ray diffraction may affect N2 selectivity because NO molecules can be dissociatively adsorbed on Pt (100), while NO is mostly adsorbed molecularly on Pt (110) and Pt (111) (García-Cortés et al., 2003). Regarding the chemical oxidation state of Pt, several researchers (Després et al., 2004; Mulla et al., 2006) reported that formation of PtO and Pt2O can degrade catalytic activity and eventually lead to deactivation of the catalyst. Another important factor determining catalytic activity is the catalyst preparation method; some materials prepared by the sol-gel method show improved activity and N2 selectivity, even in the presence of high water vapor concentrations (2.6–10%) (Seker and Gulari, 2000; Burch et al., 2002).

The Pt catalysts on metal oxide supports produced by the incipient wetness impregnation and ion-exchange methods (Burch and Millington, 1995, 1996; Burch and Watling, 1997; Burch et al., 1998; Männikkö et al., 2012) have been used to reveal that the aforementioned thermal stability problem is due to weak interactions with Pt and the supporting material. It has been established that the thermal stability issue with Pt is less severe in catalysts synthesized by the sol-gel method (Gonzalez et al., 1997; Cho et al., 1998; Romero-Pascual et al., 2002; Hu et al., 2006). Alternatively, flame spray pyrolysis (FSP) has been used for producing alumina-supported platinum catalysts (Strobel et al., 2003, 2006). More recently, the aerosol-based process has been widely investigated and used for making catalysts for deNOx (Boningari et al., 2012), deVOCs (Lin et al., 2015), deCO (Byeon et al., 2014) applications. While the aerosol methods have been recognized to be well developed, the methods have had limited success in control of agglomeration of catalysts. The uncontrolled agglomeration might reduce exposed surface areas of catalysts, leading to degradation of catalytic activity and performance.

Thus, we focused on the agglomeration/microstructural control and thermal stability of catalysts. Combining the sol-gel method with the aerosol spray-pyrolysis method (called the aerosol-gel method hereafter), we may take the unique benefits of each method (Lee et al., 2007; Firmansyah et al., 2009, 2012), together with the advantage of cost-effective production of microstructure-controlled particles (Lee et al., 1997; Santiago et al., 2011). Better understanding of the process, one can extend this method to the synthesis of binary hetero-structured catalysts.

In this study, we have applied the aerosol method for the synthesis of well-dispersed Pt particles on SiO2 and Al2O3 supports. The two types of catalysts exhibited comparable NO conversion with respect to the previous reports. The effect of sintering on particle size distribution and relevant possible mechanisms were explored.

**EXPERIMENTAL METHODS**

**Preparation of Catalysts**

A precursor solution for Pt/SiO2 catalysts was prepared as follows: 56 mg platinum (II) acetylacetone (Pt(acac)2, Aldrich, 97%) well dissolved in 33.6 mL ethanol (Aldrich, 99.5%), was mixed with 3.2 mL TEOS (Aldrich, 98%) dissolved in 17.6 mL ethanol (Aldrich, 99.5%), and the mixture solution was stirred at room temperature for 30 min. Then, 12.5 mL deionized (DI) water and 1.2 mL HCl (0.1 M) were introduced to the mixture, and then the solution was stirred at room temperature for 2 hours in order to initiate the sol-gel reaction of TEOS with water. Herein only SiO2 sols are formed, maintaining the Pt(acac)2 dissolved in the solution at low temperature.

A precursor solution for Pt/Al2O3 catalysts was prepared likewise: 40 mg Pt(acac)2 was first dissolved in 40 mL ethanol and stirred at 50°C for 30 minutes. A second solution was made by dissolving 800 mg aluminum nitrate nonahydrate (ANN, Aldrich, 98%) into 40 mL ethanol. The two solutions were mixed together, and stirred at 50°C for 30 minutes. Then, 20 mL of water and 0.1 mL of HCl (0.1 M) were introduced into the solution and stirred again under 50°C for two days.

As-prepared two different solutions were aerosolized to 1–5 µm droplets in an atomizer running with compressed air at a pressure of 25 psi and a gas flow rate of 2.2 L min−1. The droplets were therefore fed into a diffusion dryer, filled with silica gel to remove the solvent. They were then transferred to a quartz tube (1/4” in diameter), and heated by tube furnace, in which Pt(acac)2 is pyrolyzed to form tiny Pt nanoparticles. It should be noted that the droplets contain not only SiO2 sols and Pt aggregates but also remaining TEOS solution and Pt(acac)2, in the case of Pt/SiO2 catalysts. In the case of Pt/Al2O3, however, the droplets contain liquid-phase reactants of Pt(acac)2 and Al(NO3)3 until the reactant temperatures reach an adequate level in the furnace; this occurs as aluminum nitrate is never sol-gel reacted, but rather pyrolyzed at high temperature. It is noted that organic species in TEOS and Pt(acac)2 appear to leave carbon behind after the decomposition reaction when Ar was used instead of air. This is the reason why air has been used as a carrier gas.

The formation positions of solid particles (i.e., Pt with respect to its metal oxide support) can vary depending on...
the differences in their reaction kinetics. The disparity in formation timing of Pt and metal oxides enables control of the morphology in such a way that Pt dots are formed on the outer surface of the SiO$_2$ or Al$_2$O$_3$ particles. For reference (control) materials, pure SiO$_2$ or Al$_2$O$_3$ nanoparticles were also prepared in the same way as described above (without Pt source), and then examined for their performance as catalytic promoters. The residence time of particles in the furnace is estimated at approximately 0.19 s. The reacting temperature of the furnace was set to either 600°C for Pt/SiO$_2$ catalysts, or 700°C for Pt/Al$_2$O$_3$ catalysts. As-synthesized catalysts nanoparticles were collected by a glass membrane filter with 1 µm pores (Milipore). More details about experimental setup are available elsewhere (Lee et al., 2007; Firmansyah et al., 2009, 2012).

Characterization of Catalysts

As-prepared catalysts particles were dispersed in ethanol with an ultrasonicator. A few milliliters of the suspension were dropped onto a carbon-coated TEM grid and then dried in air. The size and morphology of the catalysts were observed by a high-resolution transmission electron microscope (HR-TEM; JEM 2010F & 2011, JEOL, 200 kV) equipped with an energy dispersive spectrometer (EDS). Crystalline phase of the samples was characterized in view of mole composition and crystallite size by using X-ray photoelectron spectroscopy (XPS; ESCALAB 250 XPS spectrometer) with Al K$_\alpha$ X-ray (1486.6 eV) with a resolution of 0.45 eV and X-ray diffraction (Bruker, AXS) with Cu K$_\alpha$ radiation (λ = 0.154 nm), respectively. Pt loading was measured by an inductive coupled plasma optical emission spectrometer (ICP-OES; JY ULTIMA 2 C HR, Horiba).

Test for Catalytic Activity of NO Reduction

Catalytic performance of each sample was tested as follows: each powder sample weighing 34 mg was placed inside a 1/8” diameter tube with 1 cm length, where both tube ends were blocked by a layer of glass wool. The tube inside a 1/8” diameter tube with 1 cm length, where both ends were blocked by a layer of glass wool. The tube ends were blocked by a layer of glass wool. The tube inside a 1/8” diameter tube with 1 cm length, where both ends were blocked by a layer of glass wool. A few milliliters of the suspension were added on a carbon-coated TEM grid and then dried in air. The size and morphology of the catalysts were observed by a high-resolution transmission electron microscope (HR-TEM; JEM 2010F & 2011, JEOL, 200 kV) equipped with an energy dispersive spectrometer (EDS). Crystalline phase of the samples was characterized in view of mole composition and crystallite size by using X-ray photoelectron spectroscopy (XPS; ESCALAB 250 XPS spectrometer) with Al K$_\alpha$ X-ray (1486.6 eV) with a resolution of 0.45 eV and X-ray diffraction (Bruker, AXS) with Cu K$_\alpha$ radiation (λ = 0.154 nm), respectively. Pt loading was measured by an inductive coupled plasma optical emission spectrometer (ICP-OES; JY ULTIMA 2 C HR, Horiba).

RESULTS AND DISCUSSION

Fig. 1(a) shows a typical TEM image of the as-prepared Pt/SiO$_2$ catalysts produced by the aerosol method. During the time for sol-gel reaction in the atomizer (2 hours in this study), small silica sols and aggregates were suspended in a colloidal solution, in which Pt(acac)$_2$ and a part of TEOS remained dissolved. The solution was aerosolized, subsequently heated up, and finally turned into spherical nanoparticles. Through HR-TEM characterization, it was revealed that the many tiny dark dots covering the large gray spheres were in-fact metallic Pt dots on the surface of amorphous silica spheres. Unlike the case of Pt/SiO$_2$, with Pt/Al$_2$O$_3$, two precursors of Pt(acac)$_2$ and Al(NO$_3$)$_3$ remain dissolved in the atomized droplets, until they are decomposed to solid phase at high temperatures. Nevertheless, Fig. 1(b) shows a very similar HR-TEM image of Pt/Al$_2$O$_3$ catalysts: Pt dots on large Al$_2$O$_3$ spheres. The sizes of Pt in both cases were measured and their size distributions from TEM image analysis are displayed in Fig. 1(c): more than 350 Pt nanoparticles in each case were considered and the same set of Pt particles were measured twice to yield an average diameter in an attempt to reduce the uncertainty for size.
measurement of the catalysts. As a result, the Pt dots are distributed from 1.3 to 3.5 nm in diameter, with mode diameters of 1.9 and 2.3 nm for Pt/SiO$_2$ and Pt/Al$_2$O$_3$, respectively. The larger size of Pt dots when supported by Al$_2$O$_3$ is likely attributed to higher furnace temperature, which might facilitate to sinter Pt particles into larger dots. Additionally, it can be postulated that, in the absence of sol-gel reactions which can form a matrix structure to anchor the Pt particles (Firmansyah et al., 2012), coproduced Pt dots may have a better chance to move and sinter on the surface of alumina spheres.

Of particular interest is understanding the formation mechanism of Pt dots on the surface of the metal oxide spheres, in view of size and hetero-structure of Pt particles; when a droplet evaporates during the spray-pyrolysis process, the dissolved solutes are locally concentrated near the droplet surface, and diffuse toward the center of the droplet in response to the concentration gradient, while the solvent diffuses toward the outermost region, and evaporates. It is generally accepted that the overall morphology of single-component particles is determined by the competition of solute diffusion and solvent evaporation rates (Jayanthi et al., 1993; Lenggoro et al., 2000; Lee et al., 2007). In the present study, there are two diffusing solutes in a solvent droplet: for Pt/SiO$_2$ there are non-ionic molecules of Pt(acac)$_2$ and TEOS, and for Pt/Al$_2$O$_3$, there are Pt(acac)$_2$ molecules and Al$^{3+}$ ions (from dissolved ANN). A disparity of relative diffusion speed between the solutes likely determines local abundances of the solutes, in a way that a fast diffusing solute moves toward the droplet center more quickly than a slowly diffusing solute. Noting that product particles come out of the abundant regions, the existence of Pt dots on the surface seems to indicate that the solute of Pt(acac)$_2$ is the least diffusing species. In order to confirm that the diffusion coefficients of the three solute species, as a measure of the diffusion rate, are estimated to compare as follows.

The diffusion coefficient of Al$^{3+}$ ion in a dilute solution at 298 K was determined according to Nernst-Haskell equation: $D_s = \frac{298R_g}{F^2} \left(1/\nu^+ + 1/\nu^-ight)$, where $R_g$ is the gas constant, $F$ is the Faraday constant, $\nu^+$ and $\nu^-$
are respectively the valences of the cation and anion, and $\lambda^0$ is the limiting ionic conductance (Reid et al., 1987; Firmansyah et al., 2009, 2012). In this study, the $D_s$ value for $\text{Al}^{3+}$ ions is estimated to be $1.15 \times 10^{-5}$ cm$^2$ s$^{-1}$ via $\nu_{\text{Al}^{3+}} = 3$, $\nu_{\text{NO}_3^-} = 1$, $\lambda^0_{\text{Al}^{3+}} = 59.0$ Ω$^{-1}$ cm$^2$ mol$^{-1}$ and $\lambda^0_{\text{NO}_3^-} = 71.4$ Ω$^{-1}$ cm$^2$ mol$^{-1}$. For nonionic solutes of TEOS and Pt(acac)$_2$, the corresponding values of $D_s$ are calculated by Wilke and Chang’s equation (Reid et al., 1987; Firmansyah et al., 2009, 2012):

$$D_s^0 = 7.4 \times 10^{-8} (\phi M_b)^{1/2} \eta_b V_{A}^{0.6},$$

where $M_b$ is the solvent molecular weight in g mol$^{-1}$, $\eta_b$ is the solvent viscosity in cP, $V_A$ is the molar volume of solute A at its normal boiling temperature in cm$^3$ mol$^{-1}$, and $\phi$ is the association factor. As a result, the diffusion coefficient of Pt(acac)$_2$ in ethanol is estimated to be $4.1 \times 10^{-6}$ cm$^2$ s$^{-1}$ and the diffusion coefficient of TEOS in water is estimated at $8.0 \times 10^{-6}$ cm$^2$ s$^{-1}$. It is quite clear that the lighter species of TEOS and $\text{Al}^{3+}$ diffuse to the droplet center at higher speeds, leaving behind the heaviest Pt(acac)$_2$ near the surface; this may explain why Pt(acac)$_2$ decomposes to Pt dots mainly on the surface of the silica and alumina spheres. Another route to explain the presence of Pt on the surface of the metal oxide supports is from a disparity of evaporation rates between water and ethanol. It is noted that Pt(acac)$_2$ dissolves mainly in ethanol which is 40% more volatile than water (Reid et al., 1987), while TEOS and $\text{Al}^{3+}$ dissolves in water. Hence, faster evaporation/consumption of ethanol near a droplet surface initiates the precipitation of Pt(acac)$_2$ whereas TEOS and Al(NO$_3$)$_3$ both retreat to the center along with shrinking water. This is likely how a pair of solutes is segregated.

Figs. 2(a) and 2(b) show XRD patterns of Pt/SiO$_2$ and Pt/Al$_2$O$_3$ catalysts in comparison with those of SiO$_2$ and Al$_2$O$_3$ supports only, respectively. Fig. 2(a) clearly shows four major peaks of (111), (200), (220), and (331) crystalline facets of Pt as well as a very broad peak at $\sim 23^\circ$ in 20 units. The broad peak also appears in the pure SiO$_2$ sample, indicating that the silica is almost amorphous. Likewise, Fig. 2(b) shows similar diffraction patterns of crystalline Pt on a mixture of amorphous and $\gamma$-phase alumina. Scherrer equation (Wang et al., 2006) is applied to the largest peak of Pt (111) so that the crystallite size for Pt/SiO$_2$ and Pt/Al$_2$O$_3$ are estimated as 2.8 nm and 3.1 nm, respectively, which is consistent with TEM image analysis as shown in Fig. 1(c).

The oxidation states of Pt on silica and alumina supports are examined by XPS. Fig. 3(a) shows that the Pt 4f core-level XPS spectrum of Pt/SiO$_2$ catalysts is mainly composed of three pairs of doublets. The highest doublet (at 71.2 and 74.7 eV) corresponds to metallic Pt. The second highest doublet (at 72.3 and 75.5 eV), 1 eV blue-shifted from the

![Fig. 2. XRD pattern for: a) Pt/SiO$_2$, b) Pt/Al$_2$O$_3$.](image-url)
metallic peaks of Pt, is assigned to Pt [II] states as in PtO or Pt(OH)₂. The weakest third doublet at 73.6 and 76.7 eV suggests that a minor level of Pt [IV] as in PtO₂ exists in the present catalysts (Kang et al., 2005; Choi et al., 2010). For Pt/Al₂O₃ catalysts, however, the Pt 4f core-level XPS spectrum is considerably different from that of Pt/SiO₂, mainly because the Pt 4f lines are overlapped with the Al 2p lines. Because of this interference, it is almost impossible to measure the 4f½–2 peak intensity of Pt on alumina especially when the Pt content is below 5%. Hence, the Pt 4d½–2 line is measured as an alternative (Shyu and Otto, 1988). Fig. 3(b) shows the Pt 4d½–2 core-level XPS spectrum of Pt/Al₂O₃ catalysts deconvoluted to three subpeaks. In Fig. 3(b), the highest peak at 314 eV is the signal from metallic Pt (Shyu and Otto, 1988). The second peak at 315.3 eV is assigned to Pt [II] state as in PtO or Pt(OH)₂ (Shyu and Otto, 1988). The third peak at 316.9 eV corresponds to Pt [IV], indicating the existence of PtO₂ (Shyu and Otto, 1988). The surface-oxygenated species of PtO or PtO₂ in the as-prepared Pt catalysts, which are presumably produced during the decomposition reaction at elevated temperatures of 600°C (for Pt/SiO₂) and 700°C (for Pt/Al₂O₃) in air (Hauff et al., 2012), are believed to hinder the NOx dissociation on the surface of metallic Pt (Romero-Pascual et al., 2002; Hu et al., 2006). Considering that the relative abundance of Pt, PtO, and PtO₂ is often approximated by the corresponding XPS peak area, one may notice from Figs. 3(a) and 3(b) that metallic Pt, as a major species, dominates other minor species of PtO and PtO₂. Furthermore, relative abundance of each species approximated from the surface area of deconvoluted peaks in Figs. 3(a) and 3(b), and shown in Table 1, indicates that metallic Pt⁰ is dominant for both catalysts. The value of metallic Pt⁰ reported here (73%–78%) are in good agreement with previous results for the Pt samples heat treated by flowing H₂/N₂ at 450°C (Despres et al., 2004) or N₂ at 1500°C (Kang et al., 2005).

The overall HC-SCR reaction for the produced catalysts of Pt/SiO₂ or Pt/Al₂O₃ is described as:

\[
aNO + bC_3H_6 + cO_2 \rightarrow dN_2 + eNO_2 + fN_2O + gH_2O + hCO_2,
\]

where the coefficients of \(a\), \(b\), \(c\), \(d\), \(e\), \(f\), \(g\), and \(h\) are dependent on the types of catalysts, reactant concentration, and temperature. To investigate the reaction mechanism, a compositional analysis for the mixture of the reactants and the products was performed using gas-cell FTIR. Figs. 4(a)–4(d) show FTIR spectra obtained before and after
Table 1. The relative abundance of different Pt species determined from Peak Deconvolution of XPS measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Area of relative abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/SiO₂</td>
<td>78.5 12.7 8.72</td>
</tr>
<tr>
<td>Pt/Al₂O₃</td>
<td>73.5 12.6 13.7</td>
</tr>
</tbody>
</table>

passing the reactant gases in Eq. (7) through SiO₂, Al₂O₃, Pt/SiO₂, and Pt/Al₂O₃ catalysts tested at different temperatures, respectively. FTIR spectrum at the bottom of each figure indicates a little but distinct peak of CO₂ even before contacting the catalysts. The trace level of CO₂ is believed to come from indoor atmosphere by gaseous diffusion to the gas cell of the FTIR machine. Two small double peaks at 1820–1960 cm⁻¹ are assigned to NO gas (Smith et al., 1988) and marked with a dotted box. Other peaks at 912 cm⁻¹, 1598 cm⁻¹ and 2210 cm⁻¹ are assigned to C₃H₆ (Yoon et al., 2002), NO₂ (Li and Guan, 2009) and N₂O (Sobczak et al., 2008), respectively. Though the peak of NO₂ gas is overlapped with that of H₂O (Tshilongo et al., 2009) at ~1600 cm⁻¹, it is quite clear at which temperature the NO₂ gas peak begins to be prominent in the presence of Pt (see Figs. 4(c) and 4(d)).

Figs. 4(a) and 4(b) show the spectrum of evolved gases from the catalytic support of SiO₂ and Al₂O₃ without Pt. The profiles of spectrum for 150°C and 200°C are almost the same as the inlet, implying that there is no catalytic activity of the supports in this temperature range. At temperatures of 250°C and 300°C, we observe propene combustion catalyzed by metal oxide support in which the SiO₂ support appears more active than that of Al₂O₃; this is due to the fact that NOx and O₂ cannot form an adsorbed species on the inert support of SiO₂. As a result, O₂(g) will react directly with hydrocarbon in the gas phase to generate CO₂ and H₂O when the temperature is higher than 250°C. On the other hand, NOx and O₂ can form an adsorbed species (NOads) (Burch et al., 1998) on Al₂O₃ which has higher surface acidity (Hirashima et al., 1998). In this case, hydrocarbon loses chance to react with O₂(g) in the gas phase, rather reacts with NOads at higher temperatures, and eventually generate CO₂ and H₂O. For this reason, alumina might be apparently less active than
silica for hydrocarbon oxidation. At temperatures of 350°C and 400°C, NO reduction of about 20% is observed with Al₂O₃ catalysts, while NO reduction with SiO₂ is not observed at any temperatures tested. These facts suggest that Al₂O₃ should be more favorable as a catalyst support for the NO treatment than SiO₂, and may contribute to better activity when it is combined with Pt.

For Pt/SiO₂ catalyst at 150°C, the spectrum is almost identical to that of original reactant gas mixtures (noted as ‘inlet’ in Fig. 4(c)). As temperature is increased to 200°C, the peaks of NO and C₃H₆ exhibit a slight decrease, while the peaks of N₂O and CO₂ species show distinctive increases. This suggests that NO gas is partly reduced to N₂O and N₂, and that the O from the catalyst surface might be consumed to oxidize the incoming C₃H₆ gas to generate CO₂. This is exactly how HC-SCR catalysts are supposed to function via a redox process (Burch and Millington, 1996). A dramatic change is observed in every gas species when the temperature is increased further to 250°C: a sudden disappearance of C₃H₆, associated with a huge increase in CO₂ peak, a relatively large decrease in NO peak height, a noticeable increase of NO₂ peak, and a sudden stop to change in N₂O peak. Unlike the first three observations, the fourth and fifth observations indicate that NO is not properly reduced to N₂O or N₂, but rather oxidized to NO₂ even at the expense of C₃H₆. The preferential oxidation of NO suggests that there is more abundant chemisorbed oxygen than chemisorbed nitrogen on Pt, making the oxidation more probable than reduction. A larger peak of NO₂ and a small peak of N₂O at 275°C and at 300°C were observed; the conversion of NO to NO₂ for Pt/SiO₂ at these temperatures is similar with the catalytic result as reported by Jayat et al. (1999). Moreover, the role of C₃H₆ in consuming the chemisorbed oxygen at the Pt surface becomes insignificant as the catalyst surface is almost completely covered by chemisorbed oxygen. As the temperature is increased to 350°C, the NO₂ peak and NO peaks slightly decrease, starting at this temperature, generation of gas phase NO₂ from the catalyst is limited by the NO₂ equilibrium concentration as indicated by previous authors (Seker and Gulari, 2000; García-Cortés et al., 2003). Eventually, when the temperature is increased to 400°C, C₃H₆ and N₂O almost completely disappear, suggesting that Pt oxidation is predominantly arising, which eventually leads to the degradation process.
of catalytic activity.

Similar to the Pt/SiO₂ catalyst, the spectrum for the Pt/Al₂O₃ catalyst, at 150°C, is also almost identical to that of the original reactant gas mixtures (noted as ‘inlet’ in Fig. 4(d)). As temperature is increased to 200°C and 250°C, the NO peak decreases, the C₃H₆ peak disappears, and the N₂O peak experiences a marked increase. Thus, at this temperature, NO gas is partly reduced to N₂O and N₂, and oxygen likely binds to the catalyst (Pt) surface. We observe that NO₂ gas (which indicates an oxidation process on the Pt surface) does not appear at this temperature, though C₃H₆ (which indicates a reduction process on the Pt surface) is no longer available. Thus, the Pt/Al₂O₃ catalyst appears to perform better in NOx conversion than the Pt/SiO₂ catalyst. Moreover, Pt/Al₂O₃ exhibits clearly higher peak of N₂O gas, suggesting that most of the Pt sites are likely in a reduced state promoting more NO decomposition to N₂ and N₂O. A continuous decrease of N₂O species is observed at 275°C and 300°C while NO₂ concentration is observed to increase to maximum yield of about 26% at these temperatures. In addition, the role of C₃H₆ in consuming the chemisorbed oxygen at the Pt surface over the alumina support becomes insignificant at that temperature, suggesting that the catalyst surface begins to be covered by more chemisorbed atomic oxygen. Finally, in a process similar to that of the Pt/SiO₂ catalyst, as temperature is increased further to 350°C and 400°C, the presence of C₃H₆ and N₂O is minute; suggesting that the oxidation process in Pt is again predominantly arising, which leads to the degradation of catalytic activity. And again, the decrease of NO₂ concentration at such high temperature is affected by the equilibrium concentration (Seker and Gulari, 2000; García-Cortés et al., 2003).

As explained in section 2, the degree of conversion Xₐ (refer to Eqs. (1)–(2)) for NO and C₃H₆ were measured on the basis of FTIR measurement of gas mixture before and after the gases passed through the catalysts. In addition, the as-obtained conversions of NO to NO₂ and N₂O were used to estimate the conversion of NO to N₂ on the basis of mass balance. Every corresponding conversion of each species was plotted as a function of temperature in Figs. 5(a) and 5(b) for the catalyst of Pt/SiO₂ and Pt/Al₂O₃, respectively. From both figures, C₃H₆ is rapidly consumed almost completely at

**Fig. 5.** The NOx reduction activity of: a) Pt/SiO₂, and b) Pt/Al₂O₃ catalysts.
250°C for Pt/SiO₂ and at 200°C for Pt/Al₂O₃. For NO conversion, the profile exhibits a maximum peak at 55% and 66% conversion at 300°C for Pt/SiO₂ and Pt/Al₂O₃, respectively. However, the higher NO₂ conversion of Pt/Al₂O₃ consequently produces more N₂O gas, and therefore reduces the N₂ yield (production) and N₂ selectivity. The maximum conversion of NO to N₂ for both catalysts occurs at 300°C, which corresponds to 20% and 17.5% conversion for Pt/SiO₂ and Pt/Al₂O₃, respectively. As a result, the N₂ selectivity for both catalysts abruptly increases to 50% and 31% for Pt/SiO₂ and Pt/Al₂O₃ at 250°C, respectively. In addition, the maximum yield of NO₂ is produced at the same level for both catalysts, and thus the maximum NO conversions (reduction) to N₂ + N₂O gases for both catalysts reach about 29.8% at 250°C for Pt/SiO₂, and 55.8% at 200–250°C for Pt/Al₂O₃. These facts imply that the catalytic performance of Pt/Al₂O₃ catalyst is likely better than Pt/SiO₂ catalyst in this test.

Before catalytic testing, we performed an extra heat pretreatment in an attempt to further enhance catalytic performance as Després et al. (2004) and Kang et al. (2005) did. We observe that non-pretreated samples show less NO conversion, 39% and 45% for Pt/SiO₂ and Pt/Al₂O₃ at 250°C, respectively. In order to investigate the effect of the pre-treatment on the Pt catalysts particles, we analyzed pre-heat treated samples that had been heated up to 700°C under air with a heating rate of 10 °C min⁻¹. The benefit of using air as a carrier gas is that it allows for reducing the PtO monolayer (Després et al., 2004), and increasing the size of Pt particles (García-Cortés et al., 2003; Santiago et al., 2011) to obtain the optimal size for catalytic activity.

Figs. 6(a) and 6(b) show the TEM micrograph of Pt/SiO₂ and Pt/Al₂O₃ particles after heat pretreatment. The size distribution of the pre-treated sample is shown in Fig. 6(c). Here, we recall that Fig. 1(c) shows Pt particles before sintering are homogeneously distributed in a size range of 1.1–3.5 nm, whereas the particles size distribution after sintering is widened to a range of 1–11 nm and 4–11 nm for Pt/SiO₂ and Pt/Al₂O₃, respectively. Pt particles over SiO₂ and Al₂O₃ supports appear less-dispersed than the pristine samples as seen in Figs. 1(a) and 1(b). The mode of size distribution of Pt/SiO₂ is smaller than that of Pt/Al₂O₃, suggesting that there is a stronger interaction between Pt and SiO₂ due to the initial sol-gel reactions within the precursor.

![Fig. 6. a) TEM micrograph of the pre-treated sample of Pt/SiO₂, b) TEM micrograph of the pre-treated sample of Pt/Al₂O₃, c) Histogram plot of particle size distribution for the pre-treated samples of Pt/SiO₂ and Pt/Al₂O₃.](image-url)
solution (see section 2). These reactions thereby reduce the sintering effect, and thus the dispersion of Pt particles over SiO₂ is superior to that of the dispersion of Pt particles over Al₂O₃ after sintering. Well dispersed Pt particles, with sizes larger than 2 nm may show a better NOx conversion according to previous works (García-Cortés et al., 2003; Vaccaro et al., 2003). In addition, a different Pt particle size may exhibit various reactivity to Pt, in which a higher rate of surface reaction may be observed with larger Pt crystallites, as compared to small Pt crystallites (Radic et al., 2004). However, Pt particles that are too large (> 10 nm) are less active due to weaker O bond formation (García-Cortés et al., 2003), while Pt particles that are too small are easily oxidized to PtO which is less active for NOx conversion (García-Cortés et al., 2003). Thus, a moderate size (3–8 nm) of Pt particles is recommended for efficient conversion of NOₓ (Jayat et al., 1999; García-Cortés et al., 2003; Vaccaro et al., 2003; Després et al., 2004), therefore, changing the average size of Pt particles over SiO₂ and Al₂O₃ supports from ~2 nm to larger sizes of 3.8 and 8.4 nm may contribute to the NOx conversion observed in Figs. 5(a) and 5(b).

CONCLUSIONS

Catalyst of well dispersed Pt particles over SiO₂ and Al₂O₃ supports were fabricated successfully via an aerosol method combined with pyrolysis. According to calculations for aerosol particle formation, the solute of Pt particles concentrates locally near the droplet surfaces while TEOS and Al³⁺ diffuse toward the center of the droplets, implying that Pt particles disperse on the metal oxide supports. The results of HR-TEM studies corroborate our calculations showing that the Pt/SiO₂ and Pt/Al₂O₃ catalyst particles were uniformly dispersed at the surface of each supporting material in the respective samples. The XRD patterns confirm that Pt/Al₂O₃ particle size is slightly larger than that of the Pt/SiO₂ particles. The results of XPS and peak deconvolution show that the surface of Pt/SiO₂ and Pt/Al₂O₃ are mostly covered by metallic Pt. Moreover, the maximum NOx reduction obtained for Pt/SiO₂ and Pt/Al₂O₃ catalysts are 29.8% and 55.8%, at 250°C, respectively.

The Pt particles over SiO₂ and Al₂O₃ supports from pristine catalysts before heat pretreatment are homogeneously distributed with similar particle sizes of ~2 nm. However, the Pt particles sizes are completely different at high temperature after the heat pretreatment, where the sintering effect on Pt over Al₂O₃ is more severe than that of Pt over SiO₂, suggesting that there is a stronger interaction between Pt and the SiO₂ support.

ACKNOWLEDGEMENTS

This work was supported by National Research Foundation of Korea (NRF) grants funded by the Korean Government (MEST) (No. NRF-2010-0019543). It was also supported by the Global Frontier R&D Program of the Center for Multiscale Energy Systems, funded by the National Research Foundation under the Ministry of Education, Science and Technology, Korea (No. 2012M3A6A7054863), and also by the Korea Meteorological Administration Research and Development Program under Grant KMIPA KMIPA2014-21130.

REFERENCES


Firmansyah, D.A., Kim, S.G., Lee, K.S., Zahaf, R., Kim,


Received for review, April 10, 2015
Revised, June 15, 2015
Accepted, August 19, 2015