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Catalysis Today 53 (1999) 575–582

CATALYSIS TODAY

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Characteristics of the Pd-only three-way catalysts prepared by sol–gel method

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Abstract

Pd-only three-way catalysts prepared by the sol–gel method were investigated by the three-way catalytic performance test with a simulated exhaust gas in a continuous U-tube quartz reactor at a gas hourly space velocity of 72 000 h^{-1}. The catalysts were characterized with XRD, XPS, BET surface area and pore volume. The activity and thermal stability of the Pd–Al_2O_3 catalyst prepared at pH 10 were superior to those at pH 4 during hydrolysis and condensation, which could be explained by the anchoring effect. Zr and V were found to be good promoters for the enhancement of the thermal stability and SO_2 resistance, respectively. Optimally formulated catalyst, Pd(1)–V(2)–Zr(10)–Al_2O_3, was thermally stable up to 900°C and showed a much more improved low-temperature activity and excellent SO_2 resistance. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Pd-only three-way catalyst; Sol–gel method; Thermal stability; Promoters; pH effect

1. Introduction

Since Pd metal is known to have a better resistance to thermal sintering, lower price than Pt and Rh and a good activity for the oxidation of hydrocarbon and CO [1], it is being considered as a close-coupled catalyst, which is located much closer to the engine. Therefore, it is expected to show a better activity for the removal of hydrocarbon during cold-start [2]. However, Pd is a poor catalyst for saturated hydrocarbon oxidation and selective NO reduction and shows lower resistance to sulfur than the Pt/Rh three-way catalyst (TWC).

The most practical TWC has been prepared by the impregnation method known to be a simple and economic process. In this study, we investigated the Pd-only TWC, prepared by the sol–gel method, which might provide thermal stability through the suppression of the mobility of active metal to a certain degree because of anchoring the active metals on the support [3,4]. A few studies have been reported about Pd catalysts impregnated on aerogel support as follows: the oxidation of propane [5] and the reduction of NO by CO [5], and the reduction of NO with H_2 over Pd/Al_2O_3–La_2O_3 xerogel catalyst [6,7]. However, studies on the Pd-only TWC prepared by the sol–gel method are not so many.

In the present study, we focused on the formulation of a highly stable and active Pd-only sol–gel catalyst by changing the preparation condition and using several promoters. The catalyst was characterized by XRD, XPS and BET surface area and pore volume.

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PII: S0920-5861(99)00145-5

2. Experimental

2.1. Catalyst preparation

Aluminum isopropoxide (AIP, Aldrich) was dissolved in distilled and de-ionized water to an H_2O/AIP molar ratio of 100. Then, HNO_3 (in case of pH 4) or NH_4OH (in case of pH 10) was added as a hydrolysis and condensation catalyst, followed by stirring at 50°C for 1 h. For the preparation of promoted-catalysts (Pd–M–Al_2O_3, where M denotes a promoter such as Ce, Zr and V), the precursor of each promoter (acetylacetonate form, Aldrich) dissolved in acetone was mixed with the solution and then stirred at 50°C for 1 h per promoter. Finally, palladium acetylacetonate ($Pd(AcAc)_2$, Aldrich) as a Pd precursor in acetone was added and stirred at 50°C for 4 h. Transparent gels, thus acquired, were aged at ambient temperature for 24 h and vigorously stirred until the solvent was almost removed. Drying in an oven at 110°C for 24 h, followed by calcination at 500°C for 1 h, was performed and it was designated as a fresh catalyst. Meanwhile, the aged catalyst was obtained by the treatment with air stream at 1000°C for 8 h. Palladium loading is 1 wt% and a number in parenthesis means the weight fraction of each component in all catalysts. Average particle size of fresh catalysts was $\approx$110 μm, as measured on the particle-size analyzer (Malvern instrument). A ceria-supported catalyst was prepared by solvating cerium nitrate in ammonium carbonate solution. In addition, the reference model catalyst, Pt/Rh/γ-Al_2O_3, was prepared by reducing in H_2 after successively impregnating Rh and Pt solutions on γ-Al_2O_3 (BET surface area : 160 m^2/g, Nishio). Thereafter, chloride ions, contained in the Pt precursor, were removed to ca. 0.02 wt% by flowing N_2 gas saturated with water for 10 h.

2.2. Three-way catalytic performance test

Catalytic activity data were obtained with ca. 0.2 g of a catalyst <50 mesh in a conventional fixed-bed U-tube flow quartz reactor. A simulated exhaust gas, used as a reactant, was composed of 1500 ppm NO, 0.6% CO, 500 ppm C_3H_6, 0.3% H_2, 0.6% O_2, and 13% H_2O vapor in N_2 balance with or without 30 ppm SO_2. Catalytic activity was expressed as the percent conversions of NO, CO, and C_3H_6. Conversion data were measured from 150 to 400°C with a ramping rate of 10°C/min at the stoichiometric point and the space velocity of 72 000 h^{-1}. Life-test of a catalyst was performed at 350°C for 48 h. The temperature, at which the targeting reactant (NO, CO or C_3H_6) was converted by 50%, was defined as the light-off temperature of T_{50}(°C). The catalytic activity in a wide rage of redox ratio (R) defined below was measured in the same reaction condition with the others, except that R was varied from 0.8 to 1.3 by adjusting the content of oxygen at the inlet of the reactor. The redox ratio (R) is defined as

$$R = \frac{[H_2] + [CO] + 9[C_3H_6]}{2[O_2] + [NO]}$$

when R is <1.0, 1.0, and >1.0, the composition of the feed stream is net oxidizing, stoichiometric, and net reducing, respectively. The gases were continuously analyzed by gas chromatography (CO and C_3H_6) and a chemiluminescence NO_x analyzer.

2.3. Catalyst characterization

The catalyst was characterized by a Rigaku X-ray diffractometer using Cu Kα radiation ($\lambda = 0.154$ nm) with an Ni filter. X-ray diffraction spectra were obtained by scanning at a scan rate of 4°/min. BET surface area and pore volume of a catalyst were measured by the adsorption apparatus ASAP 2010C (Micromeritics) at 77 K.

XPS spectra were acquired in the surface analysis chamber (LHS 10, SPECS GmbH, Germany). The base pressure was below 8×10^{-10} Torr and Mg Kα (10 kV, 30 mA; $E_k = 1253.6$ eV) was radiated. The kinetic energy of the ejected electrons was analyzed by a multi-channel plate in a hemispherical analyzer with the pass energy of 71 eV. The C 1s peak (284.6 eV) was used as a reference.

3. Results

3.1. Three-way catalytic performance test

Effect of acid and base catalyst during hydrolysis and condensation on the performance of Pd(1)–Al_2O_3

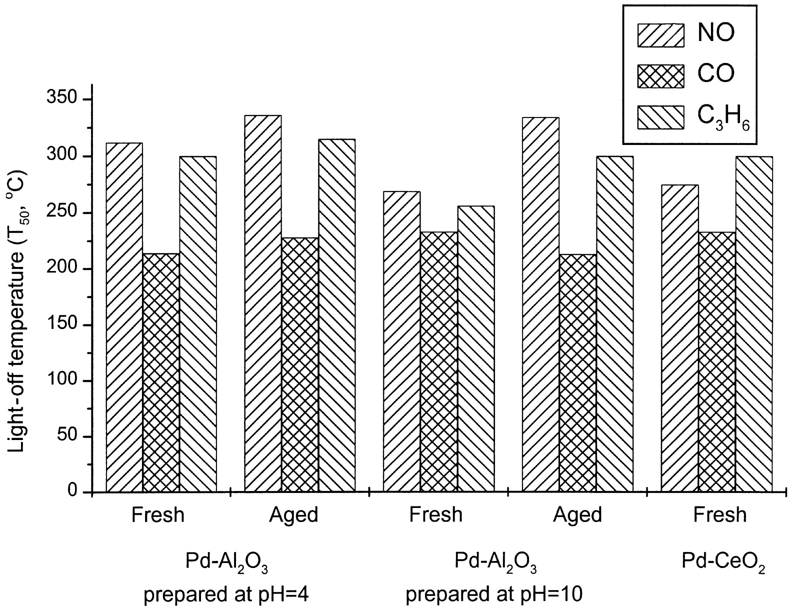

Fig. 1. T_{50} (^{o}C) for NO, CO and C_3H_6 over various catalysts prepared by the sol–gel method.

is shown in Fig. 1. In the fresh catalyst, Pd–Al_2O_3 prepared at pH 10 revealed lower $T_{50}$for NO and C_3H_6, indicating its higher activity than that prepared at pH 4. It is known that the addition of an acid increases the hydrolysis rate and, subsequently, results in more extended and less branched polymers. On the other hand, a base plays a role in enhancing the condensation rate, leading to more compact and highly branched species [3]. In our three-way catalytic reaction, Pd–Al_2O_3 prepared in the basic condition gives a better performance. After aging in air at 1000 °C for 8 h, Pd–Al_2O_3 prepared in the basic condition also showed a slightly better activity than one prepared in the acidic condition. The Pd–CeO_2 catalyst revealed lower activity than Pd–Al_2O_3 prepared in the basic condition, though it was better than that of Pd–Al_2O_3 prepared in the acidic condition.

The performances of promoted catalysts are given in Fig. 2. Pd(1)–Ce(5)–Al_2O_3 showed the highest activity for the removal of CO and C_3H_6, while Pd(1)–Zr(5)–Al_2O_3 showed highest activity for NO removal. Pd(1)–V(5)–Al_2O_3 catalyst was not deactivated by SO_2. However, Zr-promoted catalyst was severely deactivated by SO_2. In summary, Zr was a good promoter for the removal of NO, but easily deactivated by SO_2. On the other hand, V had endurance to SO_2.

The effect of V/Zr mole ratio on the conversion of NO is depicted in Fig. 3. The low-temperature activity was significantly improved on the catalysts with V/Zr mole ratio of 0.38. Accordingly, an optimal catalyst, Pd(1)–V(2)–Zr(10)–Al_2O_3, was obtained. The catalytic activity of optimal catalyst was kept after aging at 800°C and the low-temperature activity below 250°C was maintained even after aging at 900°C (Fig. 4). Moreover, its resistance to SO_2 was much higher than that of Pt/Rh catalyst (Fig. 5). The catalytic activity of optimal Pd catalyst was not significantly deactivated in the presence, and absence, of SO_2 at 350°C for 48 h.

Fig. 6 showed the effect of redox ratio on the NO conversion over various catalysts. Though the activity of the optimal catalyst was lower than that of Pt/Rh catalyst in the lean condition, it was less dependent on the variance of redox ratio than the Pd–Al_2O_3 catalysts. And its dependence on R was comparable to that of ceria-supported Pd catalyst.

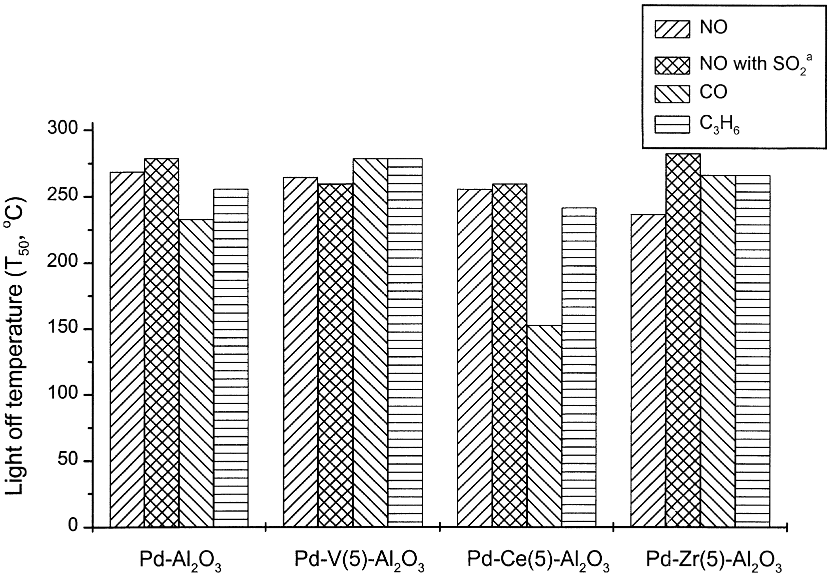

Fig. 2. T_{50}(°C) for NO, CO and C_3H_6 over various promoted Pd catalysts prepared at pH 10 during hydrolysis step. (a) In case of the stream containing 30 ppm SO_2.

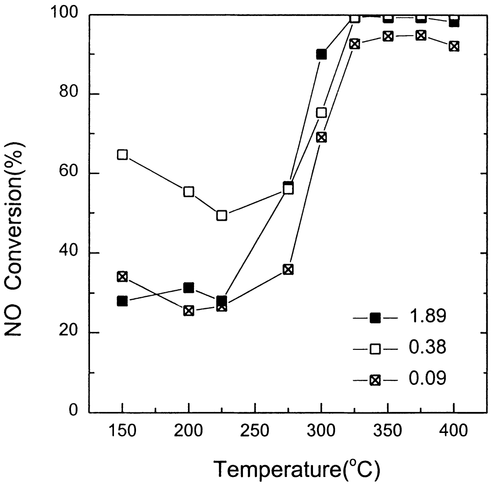

Fig. 3. Effect of V/Zr molar ratio on the NO conversion over Pd–V–Zr–Al_2O_3 sol–gel catalyst prepared in a basic condition.

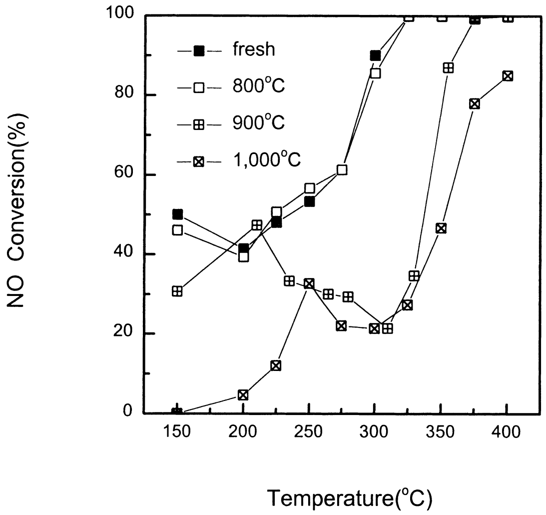

Fig. 4. Effect of aging temperature on the NO conversion over the optimal Pd–V(2)–Zr(10)–Al_2O_3 catalyst.

3.2. Catalyst characterization

3.2.1. XRD patterns

Fig. 7 shows the XRD patterns of fresh and aged Pd–Al_2O_3 catalysts. In a fresh catalyst prepared at pH 10, PdO or metallic Pd phases were not observed but a strong PdO peak came out on the catalyst prepared at pH 4, indicating its higher dispersion of Pd species than that prepared in an acid. A γ-Al_2O_3 phase was the only peak in fresh catalysts, though it was quite broad. After aging, many intense peaks appeared on both the catalysts prepared at pH 4 and 10. The most

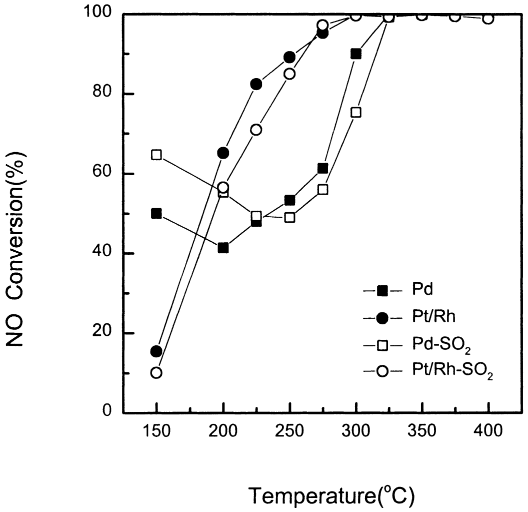

Fig. 5. NO conversion over the optimal Pd–V(2)–Zr(10)–Al_2O_3 catalyst and impregnated Pt(1)/Rh(0.2)/γ-Al_2O_3 catalyst.

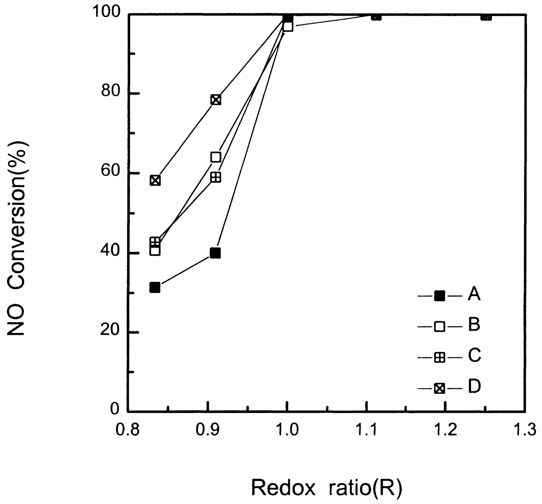

Fig. 6. Effect of redox ratio on the NO conversion over Pd–Al_2O_3 (A), Pd–CeO_2 (B), and the optimal Pd–V(2)–Zr(10)–Al_2O_3 catalyst (C) prepared in a basic condition and impregnated Pt(1)/Rh(0.2)/γ-Al_2O_3 catalyst (D) at 400°C.

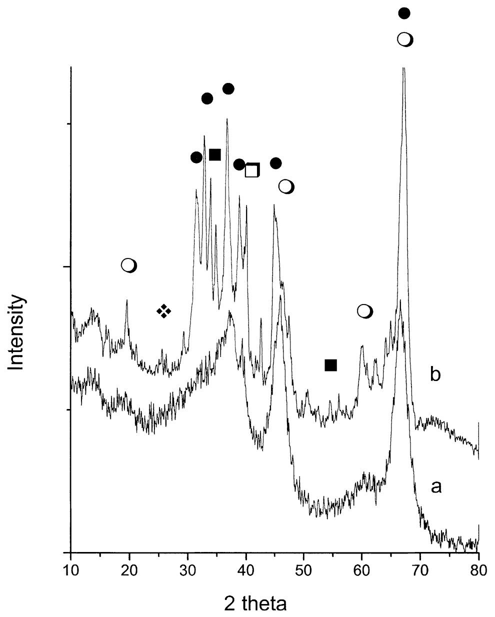

Fig. 7. XRD spectra of Pd–Al_2O_3 catalyst prepared in a basic condition (a, fresh, and b, aged). (■: PdO; ❍: γ-Al_2O_3; ❐: Pd metal; ❖: α-Al_2O_3; ●: θ-Al_2O_3).

noticeable peaks belonged to the θ-Al_2O_3 phase in the catalyst prepared at pH 10 and the θ-Al_2O_3 and α-Al_2O_3 phases in the catalyst prepared at pH 4, which were ascribed to be transformed from γ-Al_2O_3 phase. Such a transformation would result in a significant decrease of the surface area. The strong peaks at ca. 33 and 40° were assigned to PdO and metallic Pd, respectively, indicating the severe sintering to large crystalline Pd or PdO structures.

XRD patterns of catalysts containing promoters are shown in Fig. 8. The peaks corresponding to Pd species, mainly PdO, are not observed in the fresh Pd(1)–Zr(5)–Al_2O_3 and Pd(1)–Ce(5)–Al_2O_3 catalysts. Moreover, no peaks related with ZrO_2 are seen, which is in agreement with the previous study in which amorphous ZrO_2 was observed when it was prepared by the sol–gel method [8]. The fairly strong crystalline CeO_2 peaks grew enormously and many γ-Al_2O_3 phases were sintered to the α-Al_2O_3 phase on aging. However, most of the strong γ-Al_2O_3 phase were maintained and a little θ-Al_2O_3 phase and tetragonal ZrO_2 came out in the aged Pd(1)–Zr(5)–Al_2O_3 catalyst. It is significant that Zr played a crucial role in suppressing the sintering of γ-Al_2O_3 phase to α-Al_2O_3 and θ-Al_2O_3 on aging.

3.2.2. BET surface area and pore volume measurements

BET surface areas and pore volumes of Pd-only catalysts prepared by the sol–gel method are summarized in Table 1. All the fresh catalysts show larger

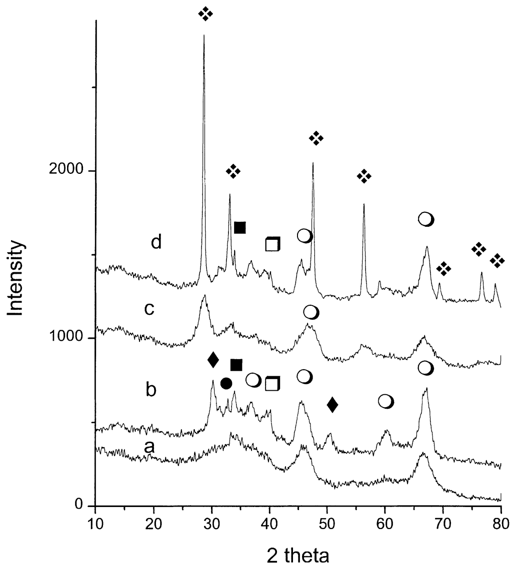

Fig. 8. XRD spectra of Pd–Zr(5)–Al_2O_3 (a, fresh, and b, aged).and Pd–Ce(5)–Al_2O_3 catalyst (c, fresh, and d, aged). (■: PdO; ❍: γ-Al_2O_3; ❐: Pd metal; ❖: CeO_2; ●: θ-Al_2O_3; ◆: ZrO_2).

Table 1

BET surface area, pore volume and average pore radius of Pd-catalysts

Catalyst Catalyst	Surface area (m^2/g)	Pore volume (cc/g)	Average Pore radius (nm)
Pd–Al_2O_3 (pH 4)			
Fresh	264.1	0.20	1.5
Aged	70.5	0.11	3.1
Pd–Al_2O_3 (pH 10)			
Fresh	315.0	0.48	3.1
Aged	116.4	0.32	5.5
Pd–Ce(5)–Al_2O_3			
Fresh	263.3	0.38	2.9
Aged	109.8	0.33	6.1
Pd–Zr(5)–Al_2O_3			
Fresh	212.2	0.33	3.1
Aged	140.3	0.35	5.0

surface areas than that by impregnation, whose normal surface area is ca. 150 m^2/g. However, it decreased drastically to ca. 70–140 m^2/g after aging. The order of surface areas of aged catalysts was in agreement with the results of XRD spectra. The highest surface area of Pd(1)–Zr(5)–Al_2O_3 after aging could be explained due to the least sintering of γ-Al_2O_3 to θ-Al_2O_3 and α-Al_2O_3 as shown in Fig. 8, whereas alumina phase of Pd–Al_2O_3 prepared at pH 4 and at pH 10 was mainly α- and θ-Al_2O_3, and θ- and γ-Al_2O_3, respectively. After aging, pore volumes decreased and average pore radius, calculated from the equation ($r = 2V/A$) increased. The pore volume, average pore radius, and, subsequently, surface area of the Pd–Al_2O_3 prepared at pH 10 were larger than that prepared at pH 4. Such properties of Pd–Al_2O_3 prepared in the basic condition are consistent with its high activity.

3.2.3. XPS spectra

XPS data are summarized in Table 2. The relative intensity of Pd/Al in Pd–Al_2O_3 prepared at pH 4 is larger than that prepared at pH 10, indicating its higher surface concentration of palladium species. After aging, the relative concentration of Pd/Al of aged Pd–Al_2O_3 prepared in an acid decreases significantly, whereas that of aged catalyst prepared in a base decreases slightly. This result suggests that most of palladium species in Pd–Al_2O_3 prepared in an acid exist on the surface and agglomerate on aging. However, palladium species in Pd–Al_2O_3 prepared in a base may be largely anchored underneath the surface and the other part of palladium is outside the surface, which is in agreement with the small peak area of palladium species, comparatively speaking, and this anchored Pd seems to be stable on aging.

Fresh Pd–Al_2O_3 catalysts have Pd $3d_{5/2}$ peaks in the range of 336.3 and 336.5 eV, which can be assigned to the PdO based on the previous data [9]. The XPS peaks of Pd–Al_2O_3prepared in an acidic condition were changed to the strong peak at 335.1 eV and the shoulder at 337.3 eV which were ascribed to the

Table 2

Binding energy of Pd $3d_{5/2}$ and relative intensity of Pd/Al in the XPS spectra

Catalyst	B.E. (eV)	Pd/Al (×100)
Pd–Al_2O_3 (pH 4)		
Fresh	336.3	8.40
Aged	335.1	2.97
	337.3	1.09
Pd–Al_2O_3 (pH 10)		
Fresh	336.5	1.67
Aged	336.1	1.51

metallic Pd and less active PdO, respectively. However, the binding energy of Pd 3d in aged Pd–Al_2O_3 prepared in a base was assigned to the PdO. XPS data suggest that a base catalyst in a sol–gel process is highly important in enhancing the thermal stability of the active metal species by anchoring.

4. Discussion

When a base is used as a catalyst for hydrolysis and condensation in a sol–gel process, the enhancement of the condensation rate, which leads to a more compact and branched species, results in a larger surface area and the formation of highly active and thermally stable Pd species [3]. Moreover, the γ-Al_2O_3 support prepared in the basic condition was not significantly sintered to α-Al_2O_3, subsequently, keeping its relatively high surface area. Also, the results of XPS implied that Pd anchoring, which seemed to enhance thermal stability, is significant for the catalyst prepared in a base.

Ceria-supported catalyst (Pd–CeO_2) showed an activity similar to that of the Pd–Al_2O_3 catalyst on the conversion of NO in spite of very low surface area. According to Cordatos et al. [10], this is attributed to an increase in free sites for the adsorption of NO, which are formed by the reduction of ceria by oxygen transfer in ceria-supported catalyst prepared by impregnation. Kim [11] reported that ceria in a TWC-promoted water–gas shift reaction and acted as an oxygen reservoir. However, Hoang-Van et al. [5] reported that ceria greatly reduced the thermal stability of Pd and Pd dispersion was significantly decreased at 600°C on the Pd catalyst containing ceria. Although ceria in Pd–Ce–Al_2O_3 played a considerable role in improving the catalytic activity, it was easily agglomerated after aging at 1000°C. It could be speculated that ceria was not stabilized by interacting with alumina or palladium in our Pd-only catalytic system. Thus, ceria should be stabilized to improve the activity and stability of Pd-only TWC in which ceria is a necessary constituent. Yao et al. [12] reported that highly dispersed ZrO_2 might be responsible for preventing the interaction between CeO_2 and Al_2O_3 support in CeO_2–ZrO_2 co-impregnated on alumina and, hence, well dispersed CeO_2–ZrO_2 was of interest as a thermally stable oxygen storage component of automotive catalyst.

Sol–gel catalyst was much more stable against SO_2 poisoning than that prepared by the impregnation method. Beck et al. [13] also reported that sol–gel catalysts were negligibly deactivated on SO_2.

BET and XRD analysis of Zr-promoted catalyst showed the high surface area of ca. 140 m^2/g and much less crystallization even after aging at 1000°C, indicating the significant contribution of Zr in enhancing the thermal stability of the Pd catalyst. Consequently, Zr-promoted catalyst showed the best activity on the conversion of NO in this study. However, we could not observe the interaction between Zr and Pd or alumina as shown by the separated Al_2O_3-and ZrO_2-only phase in Fig. 8. In the fresh catalyst, its high activity at a low temperature, below T_{50}, seems to be attributed to the existence of the weak acid site in zirconia. Levin et al. [14] reported that this might be due to the fact that alumina and zirconia, respectively, existed not as the new complex oxide form, like Al_2TiO_5 in the case of Ti-promoted alumina catalyst.

Vanadium suppressed poisoning of the catalyst by SO_2 and it was not an inhibitor but a promoter for the removal of NO. In Pd-only TWC, vanadia is an important promoter in making up for its weakness in SO_x atmosphere. However, because vanadia is easily agglomerated at high temperatures, an optimal loading of vanadium should be established. An optimal molar ratio of V/Zr in the optimal catalyst was $\approx$0.38 in this study. Optimally formulated catalyst, Pd(1)–V(2)–Zr(10)–Al_2O_3, was not nearly deactivated up to 800°C and kept its low-temperature activity even up to 900°C. Although Pd(1)–V(2)–Zr(10)–Al_2O_3 catalyst was an optimal catalyst, it showed a narrower window and lower activity above 200°C than the model Pt/Rh/Al_2O_3 catalyst. Moreover, it is required to increase its thermal stability above 900°C, which is very crucial in the application of the close-coupled catalyst. To overcome such problems, much work is being done in our group through the addition and mixing of various metal oxides [15].

5. Conclusions

The Pd catalyst prepared in a basic condition during hydrolysis and condensation of sol–gel method showed larger surface area, higher three-way catalytic activity and better thermal stability than one prepared in an acidic condition. Also, the Pd anchoring effect was significant on the catalyst prepared in a base. Zr and V were found to be good promoters for enhancing the thermal stability and SO_2 resistance, respectively. Optimally formulated catalyst, Pd(1)–V(2)–Zr(10)–Al_2O_3, was not nearly deactivated up to 800°C and kept its low-temperature activity even up to 900°C. Especially, an optimal sol–gel catalyst showed the much more improved low-temperature activity and the comparable SO_2 resistance compared with Pt–Rh/Al_2O_3 prepared by impregnation method. Pd-only TWC having good thermal stability, high low-temperature activity and strong SO_2 resistance could be prepared by the sol–gel method.

Acknowledgements

This research was funded by a national project granted from the Ministry of Commerce, Industry and Energy, and Ministry of Science and Technology (1995–1998). O-B. Yang is grateful to the Chonbuk National University for the financial support as a grant to a new faculty member in 1995.

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