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Thermally stable environmental catalyst: oxidation of methane over calcined palladium loaded on silica monolayer

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Abstract

Enhancement of thermal stability of the Pd loaded on alumina for the complete oxidation of hydrocarbons was studied by preparing the surface of a support consisting of a partially covered silica monolayer and remaining alumina by a chemical vapor deposition of silicon alkoxide. The thermal stability of the Pd-loaded silica-deposited alumina was tested after the calcination at 1493 K. The silica monolayer not only maintained the high surface area, but also suppressed the sintering of palladium. After the calcination, the catalytic activity of Pd/10 wt% SiO_2/Al_2O_3 was double that on Pd/Al_2O_3, although it decreased to 1/10 of the initial activity. The support and loaded palladium were characterized by BET, XRD, TEM and TPR measurements.

Keywords: Methane; Combustion; Palladium; Silica; Alumina; Thermal stability; Chemical vapour deposition

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1. Introduction

Catalytic combustion of hydrocarbons has recently been studied to facilitate the removal of harmful or odor hydrocarbons in order to protect the atmospheric environment. High and durable catalytic activity will therefore be required, since the environmental catalyst will be used under unusual and serious conditions. Although the Pd loaded on alumina catalyst was proposed as an active catalyst for the combustion of hydrocarbons [1–5], the sintering of palladium metals during the reaction is a fatal problem. Current investigations to develop the environmental combustion catalyst therefore concern the development of durable metal-loaded catalysts: the high surface area of the support and anti-sintering of the loaded metals on it will be the targets of the investigations.

We have already studied the combustion of methane on Pt [6] or Pd [7] loaded catalysts. In both cases, the surface of loaded metal is actually oxidized, and the oxide form of the metal plays the role of the active site. However, platinum and palladium loaded on the support have contrary conditions of effects by the support; platinum is active on the support with the strong acidity [6,8], while palladium is active on the non-acidic support, like silica [7]. Different conditions of the metal surface are required for the oxidation of methane. Another important character of palladium is ready sintering during the reaction. Although palladium is more active than platinum, at least in the oxidation of methane, the problem of sintering of palladium has to be solved.

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Adding barium cation to the alumina has been reported to maintain the high surface area when it is calcined at high temperatures [9]. A relationship between the size of alkaline and alkaline earth cations and the maintained surface area has been reported [10]. On the other hand, the addition of silica also is effective in maintaining the high surface area [11,12]. Our previous investigation on the alumina modified by silica deposited by a method of chemical vapor deposition (CVD) showed that a silica monolayer enhanced the thermal stability of alumina, but excess amounts of silica deposited brought about the loss of surface area [13]. The chemical vapor deposition from silicon alkoxide is an effective method in preparing the monolayer on alumina, as has been previously reported [14].

Based on these investigations, our present strategy in improving the catalyst activity will be directed to two kinds of effects caused by the silica monolayer. First, the support for palladium metals will be prepared by designing the support surface consisting of alumina and silica, separately. In this case, silica will play a role to prevent metals from sintering due to the steric hindrance. Second, the extremely high thermal stability of the silica monolayer on alumina will be utilized for loading of palladium in order to obtain the thermally stable palladium catalyst. Oxidation of methane will be used as a test reaction of the catalysts.

2. Experimental

Alumina, supplied by the Catalysis Society of Japan, JRC-ALO4, was modified by a chemical vapor deposition of tetramethoxysilane [$Si(OCH_3)_4$] at 593 K. The method of CVD has been described in detail elsewhere [14]. Palladium supported catalysts were prepared by the impregnation method. Alumina, modified or unmodified, was added to the solution of $PdCl_2$, and heated on a hot plate until excess water had evaporated. After drying at 383 K, it was heated at 773 K for 3 h in a flow of nitrogen. The loading of Pd was 0.5 wt%.

Catalytic activity for the oxidation of methane was measured by the continuous-flow method. Gas mixture of $CH_4/O_2/N_2$ (1:2:7) was fed at 100 ml/min into the Pyrex glass reactor in which 0.01 g of catalyst diluted with 1 g of glass bead was installed, and the products were analyzed by gas chromatography with Molecular Sieves 13 X and Porapak Q columns both operating at room temperature. The thermal stability was tested, after the catalyst was calcined at 1493 K for 24 h in a furnace, where no stream of air was supplied.

Adsorption of CO was made by a pulse method at room temperature.

Temperature programmed reduction (TPR) was measured using the all-glass apparatus with the thermal conductivity cell. After the sample was oxidized in an oxygen flow at 873 K, the bed temperature was then cooled down to dry-ice temperature, 203 K, and the carrier gas was switched to 60 cm^3 min^{-1} of $Ar–H_2$ mixture gas (6 vol% H_2). The bed temperature was then increased at a rate of 10 K min^{-1} up to ca. 573 K.

Transmission electron microscopy (TEM) image was measured by Hitachi Model H-800, where the applied voltage was 200 kV.

3. Results and discussion

3.1. Design of support surface for anti-sintering of Pd by the deposition of silica

Usually, palladium metals are loaded on alumina surfaces in preference to silica ones, as can be seen from the previous measurements of dispersion [7]. On the other hand, a silica monolayer can be prepared by the chemical vapor deposition of silicon methoxide, as has been previously reported by us [13,14]. When patches of silica monolayer are formed on the surface of alumina with less than 100% coverage, there are two individual fractions of alumina and silica

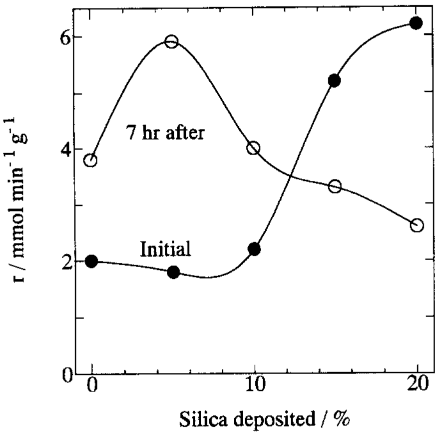

Fig. 1. Change of activity of Pd loaded on SiO_2 deposited on alumina: ●, in the beginning; ○, after 7 h on stream.

surface. When palladium is loaded on the incompletely silica-coated alumina surface, palladium will be loaded on the exposed alumina, and the sintering of palladium metals would be suppressed due to the steric hindrance by the nearest silica.

In order to prove the strategy, the palladium loaded on the silica-deposited alumina was prepared and used for the methane oxidation. Fig. 1 shows the activity in the beginning and after 7 h on stream where it was nearly stabilized or still decreasing. The activity of palladium on the alumina increased in the beginning, attained the maximum, and gradually decreased with time-on-stream. The low activity in the beginning conditions is due to the strong effect caused by the alumina support on the well-dispersed palladium, and the subsequent decrease in the activity to the decease in the dispersion of palladium metals. The behavior, however, changed by the deposition of silica. The activity decreased simply with time-on-stream, on the Pd/15 to 20 wt% SiO_2 deposited on alumina. Because the amount of 15–20 wt% of silica was close to 100% coverage by silica, the decrease in activity was not different from on the Pd/SiO_2 [7]. On the other hand, the activity of Pd on the 5–10 wt% silica deposition was similar to on alumina in the beginning, but this had more durable activity than on alumina. In particular, the Pd on 5 wt% SiO_2 on Al_2O_3 had the highest durable activity among them, where the coverage by silica was ca. 25%. Palladium may be loaded on the alumina which owns ca. 75% of the surface, and its sintering may be suppressed by the silica deposited. Control of the surface of alumina by the deposition of silica thus creates the unique discriminated surface which is available for loading durable palladium metals.

3.2. Thermal stability and activity of Pd on the silica deposited on alumina

We then checked the thermal stability of the Pd on the SiO_2/Al_2O_3 thus developed. The catalyst was calcined at 1493 K, and used for the oxidation of methane at 723 K. Fig. 2 shows the activity of the calcined Pd-loaded catalyst against the amount of deposited silica. By the calcination at 1493 K, the activity of methane oxidation dropped significantly down to 1/10 to 1/20 of the uncalcined sample activity, but it was stabilized almost completely. The Pd on 10 wt% SiO_2 deposited Al_2O_3 had the maximum activity with respect to the amount of silica loading, while the most durable activity was observed on the 5 wt% SiO_2 deposited before the calcination. The silica deposited on alumina kept the activity, even after the calcination, and

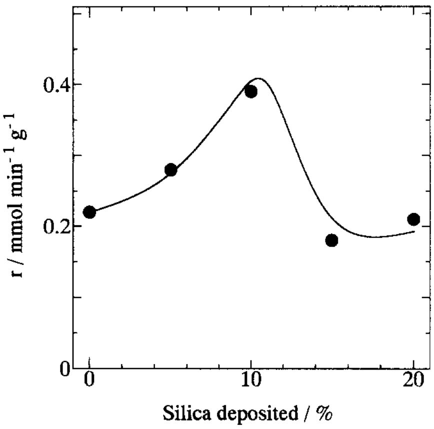

Fig. 2. Activity for the methane oxidation of Pd on SiO_2 deposited on alumina at 723 K after the calcination at 1493 K against the amount of deposition.

the activity attained was almost double that on usual alumina.

3.3. Characterization of Pd loaded on SiO_2/Al_2O_3

3.3.1. Surface area and XRD

The support and loaded palladium of catalysts was then characterized using various techniques.

Fig. 3 shows the surface area of these catalysts after the calcination at 1493 K. Although the surface area of alumina support was low (4 m^2 g^{-1}), the addition of silica maintained the high surface areas. In other words, the sintering of alumina support was suppressed by the deposition of silica. The maximum surface area was found on the 15 wt% of SiO_2 deposited on alumina. The relationship between the surface area and the amount of SiO_2 loading was in agreement with on the Pd-unloaded SiO_2 deposited alumina [13]. In other words, the loading of Pd metals did not affect the behavior of sintering of the support, SiO_2/Al_2O_3.

From our previous study [13], it was found that the monolayer of silica retarded the sintering of alumina, and the deposition of excess amounts of silica resulted in the loss of surface area. The surface of calcined catalyst was covered by a silica monolayer with the alumina surface almost completely covered. Because the 5 and 10 wt% silica deposited on alumina had 11 and 20 Si nm^{-2} of the surface concentration, respectively, and the cation site density of the alumina surface was estimated to be 13 nm^{-2}, the surface of these samples was almost completely covered by the silica monolayer.

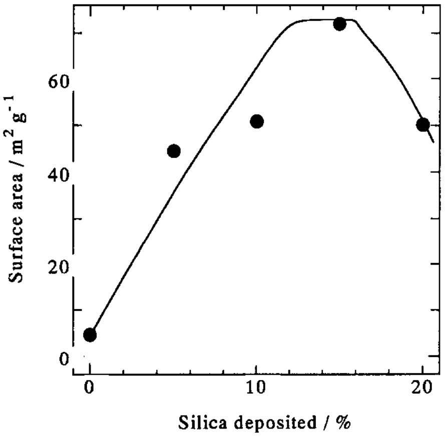

Fig. 3. Surface area of the catalyst after the calcination at 1493 K.

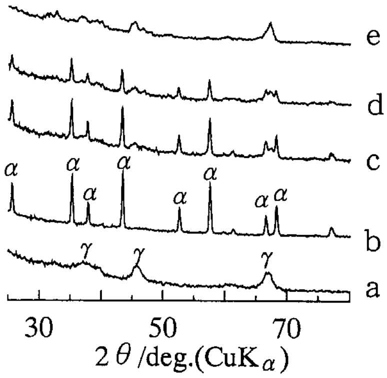

Fig. 4. XRD of the calcined catalysts: a, alumina uncalcined; b–e, calcined samples; b, alumina; c, 5 wt%; d, 10 wt%; e, 15 wt% SiO_2 on alumina.

Fig. 4 shows the XRD of the calcined catalyst. The γ-phase of uncalcined alumina changed into α-phase after the calcination. However, the sample of 15 wt% SiO_2 deposited Al_2O_3 which had the highest surface area did not show clear diffractions of the α-phase. Although the diffraction pattern was not clearly identified, the meta-stable phase of alumina γ to α seemed to be included in the samples of 10–15 wt% SiO_2 deposition. The XRD pattern thus supported the anti-sintering behavior of alumina support by the addition of silica.

3.3.2. TEM, CO chemisorption and TPR for Pd

Fig. 5 shows the photographs obtained from the transmission electron microscope for the Pd loaded on unmodified and silica-deposited alumina catalysts before and after the calcination. Although it was not easy to identify the particles of palladium, some dots of metals could be observed, particularly after the calcination. However, the change of morphology of the alumina catalyst by the calcination is very clearly identified in Fig. 5b. The agglomeration into large particles of α-alumina was noticeable

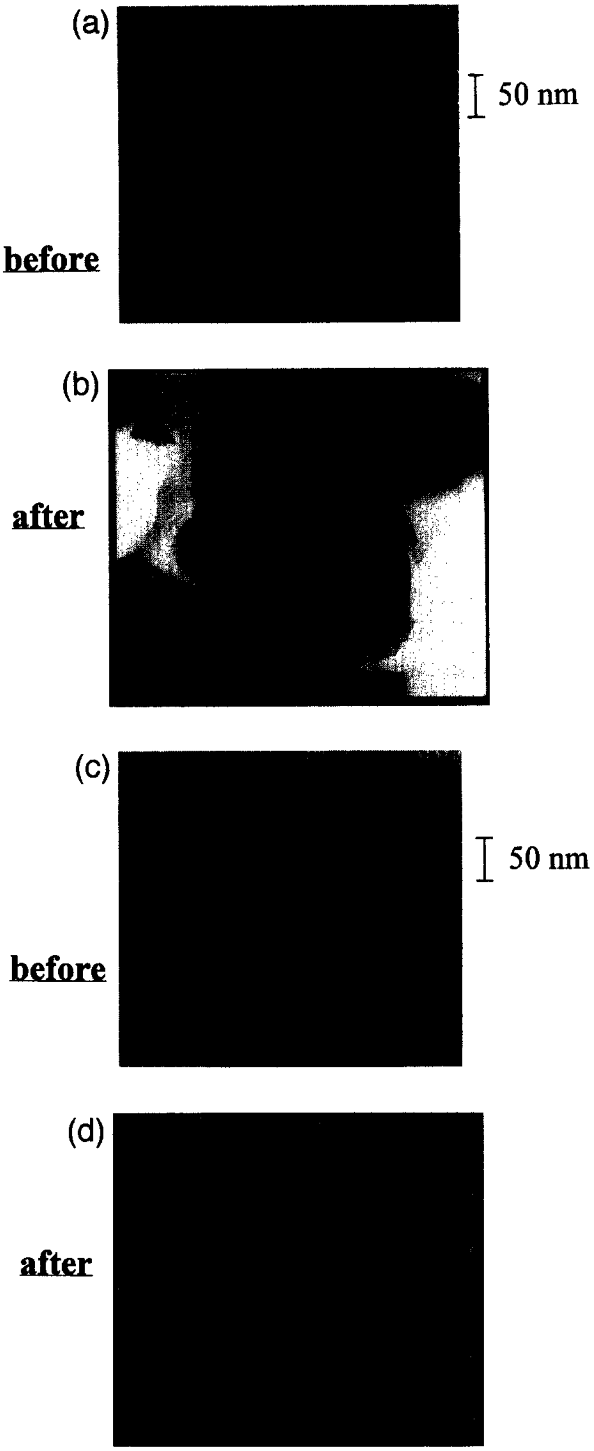

Fig. 5. TEM photographs of uncalcined (a,c) and calcined (b,d) catalysts: a,b, Pd/Al_2O_3; c,d, Pd/10 wt% SiO_2 on Al_2O_3.

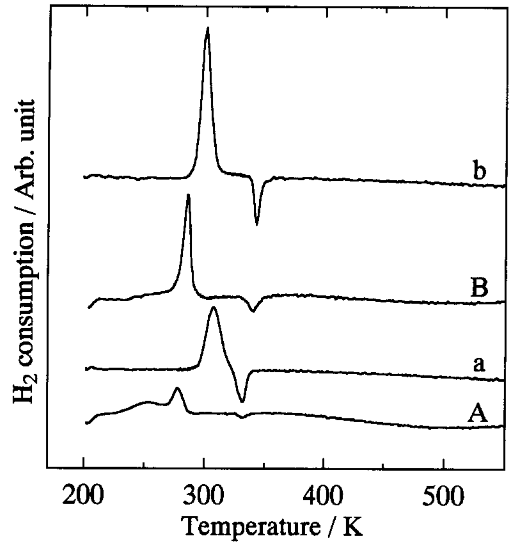

Fig. 6. TPR of Pd on Al_2O_3 (A,a) and on 5 wt% SiO_2 on Al_2O (B,b) before (A,B) and after (a,b) the calcination.

after the calcination of alumina. The particle sizes of Pd loaded on the 10 wt% SiO_2 on Al_2O_3 before and after the calcination were ca. 5 and 20 nm, respectively.

The dispersion of Pd on 10 wt% SiO_2 on Al_2O_3 before the calcination was 20%, and the estimated size of Pd, 7.5 nm, approximately agreed with the sizes of particle measured by TEM measurements (5 nm). However, the amount of CO chemisorption on Pd loaded on the support cannot be measured after the calcination; it was too small to be measured quantitatively.

Temperature programmed reduction experiments were then carried out on the calcined and uncalcined samples. Fig. 6 shows the TPR on Pd/Al_2O_3 and Pd/5 wt% SiO_2 on Al_2O_3 before and after the calcination. TPR showed small and large consumption peaks of hydrogen at ca. 210–250 and 280–300 K. Additionally, an inversion peak was observed at 340 K. These were named 1st, 2nd and 3rd peaks; the intensity and the temperature are summarized in Table 1.

Palladium oxide was able to be reduced at such a low temperature as ca. 210 K, and the high reducibility of Pd–O seemed to be effective in the methane oxidation. It is interesting that the intensity of the 1st peak could be correlated with the catalytic activity, since the activity shown in Fig. 2 and the intensity of the 1st peak showed a similar dependence upon the amount of silica deposited.

On the other hand, the 2nd peak could be ascribable to the reduction of the bulk palladium oxides, and the third one to the desorption of hydrogen from palladium hydride. We could suspect the conditions of Pd from these behaviors in the TPR experiment.

The ratio of H_2/Pd of the calcined samples was much less than 1 or 2 which was expected from the formation of PdO or PdO_2. Because it

Table 1
Intensity and temperature of TPR for the calcined and uncalcined catalysts before the reaction

SiO2 wt% [a]	1st peak		2nd peak		3rd peak		H_2/Pd
	Intensity [b]	Temperature [c]	Intensity	Temperature	Intensity	Temperature	
0c	0.17	206	32	306	−7.7	331	0.52
5c	0.58	212	30	300	−6.8	343	0.50
10c	0.85	208	30	297	−6.9	342	0.51
15c	0.52	210	18	305	−5.6	342	0.27
20c	0.56	208	7.4	280, 297	−2.1	346	0.12
0u	5	253	11.2	278	−0.7	331	0.33
5u	0.9	213	31	285	−3.8	341	0.60
0u [e]	2	209	64	278	−6.6	338	1.25

[a] c, calcined, u, uncalcined samples.
[b] Intensity shown in mmol g-cat^{-1}.
[c] Tempeature in K
[e] 7 h after the reaction.

was 1.25 on the Pd/Al_2O_3 which was uncalcined and used for 7 h in the reaction, the small value indicated the inactivation of palladium by the interaction with the support or by the covered silica. The shift of second peak to high temperatures by the calcination, e.g., from 278 to 306 K on alumina, also showed the qualitative change of Pd. No evaporation of palladium was confirmed by an XRF experiment, because it showed similar intensities before and after the calcination. Thereby, it may be deduced that the low value of H_2/Pd on the calcined samples of alumina and less than 10 wt% of SiO_2 deposition is due to the qualitative change of palladium by the calcination. In addition, on the calcined samples of more than 15 wt% SiO_2 with the silica overlayer exceeding to the monolayer, some of the palladium seemed to be covered with the silica after the calcination.

4. Conclusion

Silica monolayer which partially covered the surface of alumina support not only enhanced the thermal stability, but also retarded the sintering of palladium. The thermal stability was embedded due to the formation of a tough silica monolayer on alumina, and the sintering of palladium was suppressed due to the steric hindrance by the nearest silica, as shown by the scheme in Fig. 7. While the high surface area of support was maintained even after the high temperature calcination, the activity decreased to 1/10 of the initial activity because of not only the formation of large palladium, but its qualitative change. The most thermally stable catalyst for the methane oxidation was, however, obtained on the 10 wt% silica deposited on alumina. The activity of the catalyst was about twice as much as on the catalyst loaded on usual alumina.

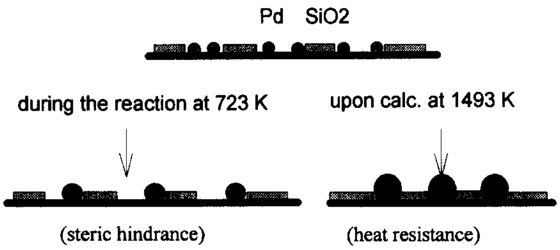

Fig. 7. Model of the Pd on 10 wt% SiO_2 deposited on Al_2O_3: change of morphology and sintering of Pd during the reaction and upon calcination at 1493 K.

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References

[1] C.F. Cullis, D.E. Keene and D.L. Trimm, Trans. Faraday Soc., 67 (1971) 864.
[2] R.F. Hicks, H. Qi, M.L. Young and R.G. Lee, J. Catal., 122 (1990) 295.
[3] A.B. Kooh, W.-J. Han, R.G. Lee and R.F. Hicks, J. Catal., 130 (1991) 374.
[4] R. Burch and P.K. Loader, Appl. Catal., B, 5 (1994) 149.
[5] F.H. Ribeiro, M. Chow and R.A. Dalla Betta, J. Catal., 146 (1994) 537.
[6] M. Niwa, K. Awano and Y. Murakami, Appl. Catal., 7 (1983) 317.
[7] K. Muto, N. Katada and M. Niwa, Appl. Catal., A, 134 (1996) 203.
[8] A. Ishikawa, S. Komai, A. Satsuma, T. Hattori and Y. Murakami, Appl. Catal., A, 110 (1994) 61.
[9] M. Machida, K. Eguchi and H. Arai, J. Catal., 103 (1987) 385.
[10] J.S. Church, N.W. Cant and D.L. Trimm, Appl. Catal., A, 101 (1993) 105.
[11] B. Beguin, E. Garbowski and M. Primet, J. Catal., 127 (1991) 595.
[12] T. Mori, T. Horiuchi, T. Iga and Y. Murase, J. Mater. Chem., 2 (1992) 577.
[13] N. Katada, H. Ishiguro, K. Muto and M. Niwa, Adv. Mater., Chem. Vap. Deposit. 1 (1995) 55.
[14] M. Niwa, N. Katada and Y. Murakami, J. Phys. Chem., 94 (1990) 6441.