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Alumina–silica aerogel catalysts prepared by two supercritical drying methods for methane combustion

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Palladium-supported alumina–silica (10 mol %) aerogels were prepared by two different supercritical drying methods. In one method, an alumina–silica wet gel was dried under supercritical conditions of ethanol in an autoclave at a temperature of 270 °C and pressure of 26.5 MPa. In the other, ethanol was supercritically extracted by carbon dioxide in an extractor at 80 °C and 15.7 MPa. Their catalytic properties for methane combustion were measured after being fired at 1200 °C for 5 h. The palladium-supported alumina–silica aerogels prepared in the autoclave showed higher activity (methane conversion) than the one prepared in the extractor. This was attributed to the autoclave-dried aerogel having a larger pore size and better palladium dispersion.

1. Introduction

Recently, alumina aerogels have been fabricated and their properties examined [1]. Palladium- and platinum-supported alumina aerogels have also been prepared in an autoclave at a temperature of 270 °C and pressure of 26.5 MPa. The catalytic activity of these aerogels for methane combustion has been evaluated [2]. It was found that the alumina aerogel catalysts exhibited much more activity than a commercial alumina with palladium catalyst prepared by the conventional dipping method. The palladium-supported alumina aerogels were then prepared by another method, using supercritical extraction with carbon dioxide (CO_2) in a CO_2 extractor at 80 °C and 15.7 MPa [3]. This alumina aerogel catalyst formed in this manner was then fired at 1200 °C for 5 h and its activity for methane combustion evaluated. The aerogel catalyst exhibited fairly good activity for methane combustion.

Maintaining high surface area at high temperatures is a very important characteristic for a methane combustion catalyst [4, 5]. Both the catalyst and support are exposed to temperatures of more than 1000 °C in a catalytic combustion system. Alumina–silica (10 mol %) aerogels have a higher specific surface area than the alumina aerogel [6]. Therefore, in the present study, palladium-supported alumina–silica (10 mol %) aerogel catalysts were fabricated by two different supercritical drying methods and tested for methane combustion.

2. Experimental procedure

Fig. 1 shows a flow chart of the procedure to synthesize the palladium-supported alumina–silica aerogels. Tetraethylorthosilicate (TEOS) in ethanol was partially hydrolysed with water ($TEOS:H_2O = 1:1$). The partially hydrolysed TEOS and alumina sec-butoxide ($Al(OBu^{sec})_3$) were mixed ($Al:Si = 90:10$), with the reaction creating Al–O–Si bonds [7]. Ethyl acetoacetate (etac) was added to yield an $Al(OBu^{sec})_3$-etac complex ($Al(OBu^{sec})_3:eatc = 1:1$) to control the speed of hydrolysis. This mixture was then hydrolysed with water diluted by ethanol. Palladium chloride with pyridine was added to the hydrolysed alumina–silica sol. The palladium chloride and pyridine yielded a complex which prevented the precipitation of palladium metal [2]. The alumina–silica sol containing palladium (1 wt % as metal) was maintained for a week at 60 °C to facilitate the gelation and ageing processes. Samples of the alumina–silica wet gel were then dried under the supercritical condition of ethanol, using an autoclave at a temperature of 270 °C and pressure of 26.5 MPa. In the other method, samples were dried by extraction with CO_2 in the supercritical state at 80 °C and 15.7 Pa, using a CO_2 extractor.

The palladium-supported alumina–silica aerogels were then fired at 1200 °C for 5 h. The aerogels were broken into 2–3 mm grains, packed into a quartz tube which was placed in a fixed-bed flow reactor. A gas mixture consisting of 1 vol % methane and 99 vol % air was flowed into the quartz tube. Space velocity was set at $30\,000\ h^{-1}$. The combustion reaction of the methane was induced by heating. The gases that evolved through combustion were analysed by gas chromatography (GC-8A; Shimadzu Co.).

The crystalline phases of the aerogels were determined by X-ray powder diffraction patterns (XRD: RAD-II,

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Rigaku Co.). The specific surface areas of the aerogels were determined by the single-point BET method using nitrogen (Monosorb, MS-15; Quantachrome), while the pore-size distributions of the aerogels were measured using a mercury porosimeter (Parameritics Co.). Morphologies of the aerogels were observed using a scanning electron microscope (JSM-840A, Jeol) and a transmission electron microscope (JEM-200CX, Jeol). The support and catalyst surfaces were analysed using Auger electron spectroscopy (JAMP30, Jeol).

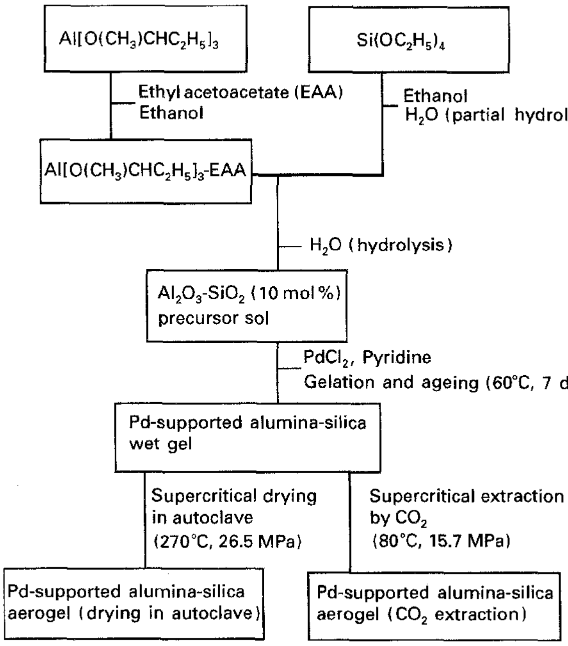

Figure 1 Flow chart of the procedure to synthesize the palladium-supported alumina–silica (10 mol %) aerogels.

TABLE I Specific surface area (SSA), porosity, and bulk density of palladium-supported alumina–silica aerogels

	SSA ($m^2 g^{-1}$)	Porosity (%)	Bulk density ($g cm^{-3}$)
Aerogel catalyst I	93.20	62.1	0.95
Aerogel catayst II	69.32	39.2	1.94

3. Results

Table I lists the specific surface area, porosity, and density of the palladium-supported alumina–silica (10 mol %) aerogels. The aerogel catalysts maintained high specific surface areas. The palladium-supported alumina–silica aerogel prepared in the autoclave (aerogel catalyst I) exhibited a specific surface area of 93.2 $m^2 g^{-1}$, while that prepared in the CO_2 extractor (aerogel catalyst II) measured 69.3 $m^2 g^{-1}$. The porosity of aerogel catalyst I was 62% and aerogel catalyst II was 39%. These results show that both the aerogel catalysts maintained a porous structure after firing at 1200 °C for 5 h.

Fig. 2 shows scanning electron micrographs of the aerogel catalysts I and II. The surface particles could be clearly observed in aerogel catalyst I (Fig. 2a). The particles found in aerogel catalyst II (Fig. 2b) appear to be more sintered although profiles of the particles could be detected. These morphologies corresponded to the data given in Table I. The degree of grain growth was almost the same in both catalysts, while the packing density was higher in aerogel catalyst I.

Fig. 3 shows transmission electron micrographs of the aerogel catalysts fired at 1200 °C for 5 h. The morphologies are similar; no palladium particles are observed in these micrographs.

The X-ray diffraction patterns of the aerogel catalysts are shown in Fig. 4. The crystalline phase of aerogel catalysts I and II was assigned to the γ phase. For palladium, the phases of Pd (1 1 1) and (2 0 0) are clearly observed at 40.1° (2θ) and 46.5°, respectively, in the XRD pattern of aerogel catalyst I (Fig. 4a). Those of aerogel catalyst II are also detected (Fig. 4b); however, they are almost obscured by other peaks. The peak for PdO (1 0 1) could be observed at 33.8° (2θ) in aerogel catalyst I, but was not observed in the aerogel catalyst II. This indicates that

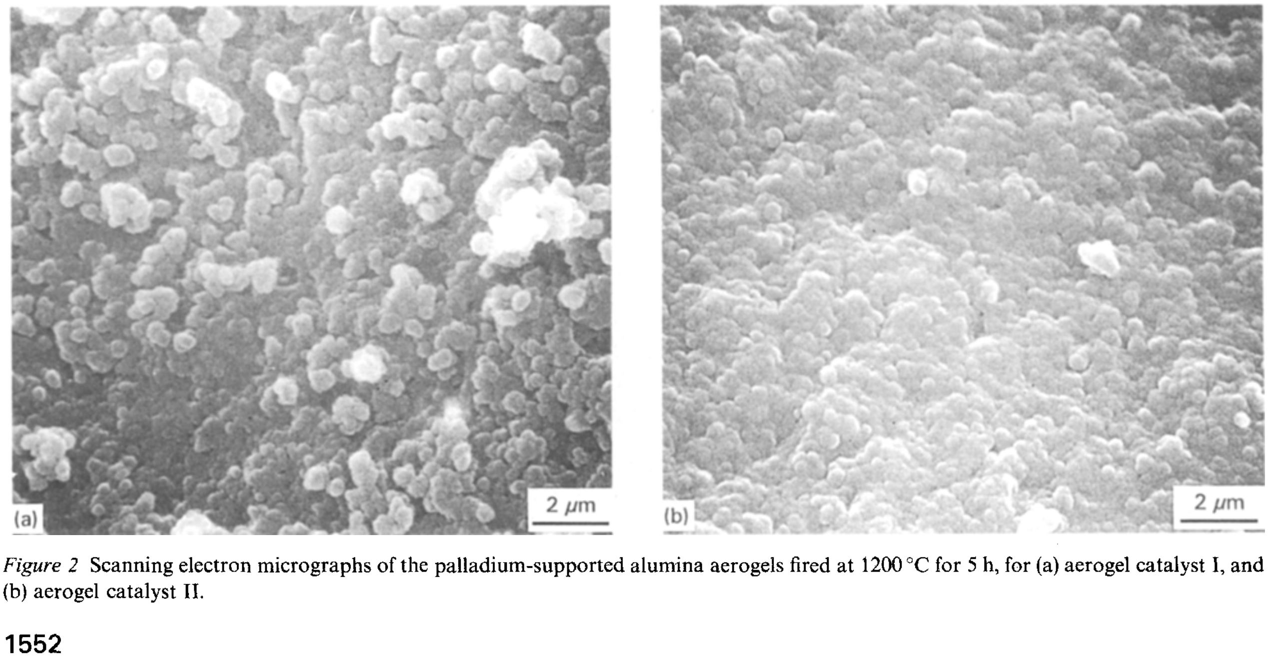

Figure 2 Scanning electron micrographs of the palladium-supported alumina aerogels fired at 1200 °C for 5 h, for (a) aerogel catalyst I, and (b) aerogel catalyst II.

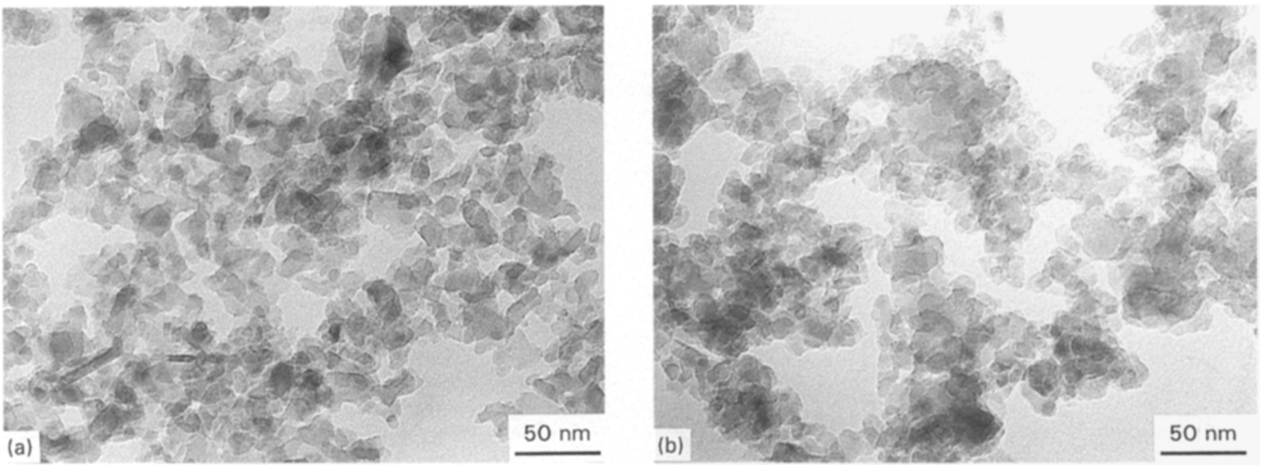

Figure 3 Transmission electron micrographs of palladium-supported alumina aerogels fired at 1200 °C for 5 h: (a) aerogel catalyst I, and (b) aerogel catalyst II.

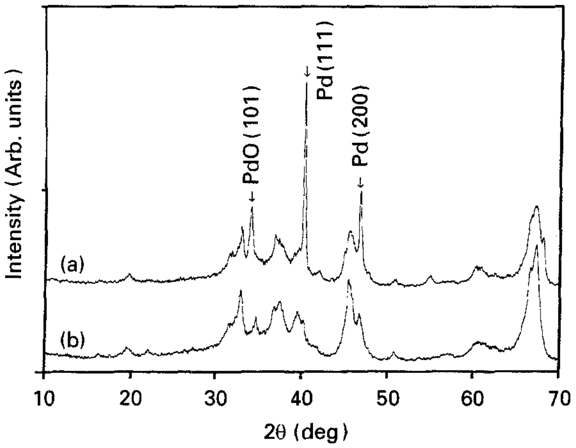

Figure 4 XRD patterns of palladium-supported alumina aerogels fired at 1200 °C for 5 h, for (a) aerogel catalyst I, and (b) aerogel catalyst II.

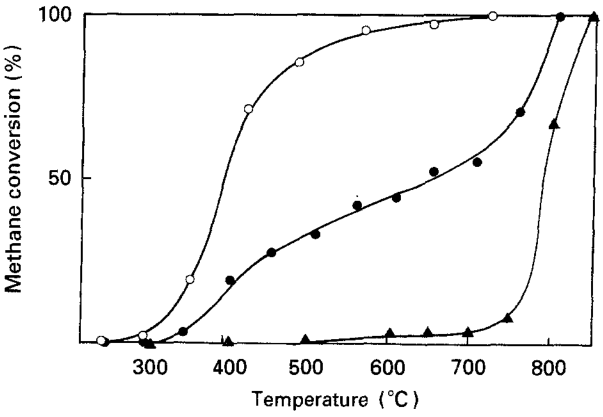

Figure 5 Catalytic activity (methane conversion) as a function of temperature for the palladium-supported alumina aerogels fired at 1200 °C for 5 h. (○) Aerogel catalyst I, (●) aerogel catalyst II, (▲) the thermal reaction without a catalyst.

the palladium crystallites found in aerogel catalyst II differ from those in aerogel catalyst I.

Fig. 5 shows the catalytic activity (methane conversion) as a function of temperature of the aerogel catalysts for methane combustion. Aerogel catalyst I exhibits more activity than aerogel catalyst II. The activity of aerogel catalyst II followed that of the aerogel catalyst I to temperatures around 300 °C. However, at temperatures greater than 400 °C, the activity of aerogel catalyst II did not increase to the extent shown by aerogel catalyst I. The temperature of perfect combustion (100%) for aerogel catalyst II was close to that of the thermal reaction.

Fig. 6 displays the pore-size distributions of both aerogel catalysts. Aerogel catalyst I exhibited a relatively broad pore size distribution, having an average pore size of 20.8 nm (Fig. 6a). On the other hand, aerogel catalyst II has a narrow pore-size distribution with an average pore size of 8.6 nm (Fig. 6b).

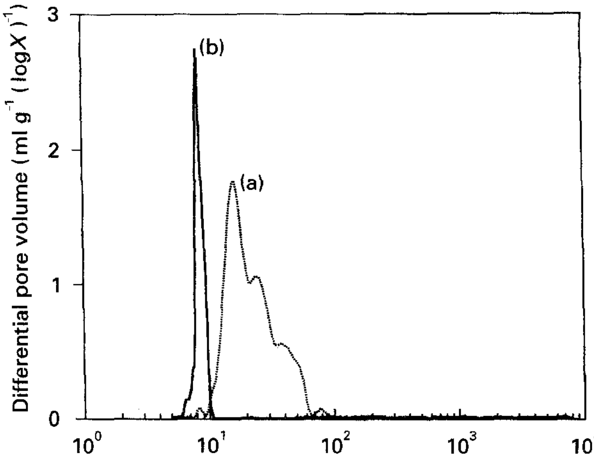

Figure 6 Pore-size distributions of palladium-supported alumina aerogels fired at 1200 °C for 5 h: (a) aerogel catalyst I, and (b) aerogel catalyst II.

Fig. 7 shows the AES spectra of the palladium on the surface of the aerogel catalysts. The peaks displayed at 328 eV correspond to the *MNN* transition of palladium. Both profiles have almost the same shape. No difference in the chemical shift of palladium was found in either profile. No substances except aluminium and palladium, or contamination from the

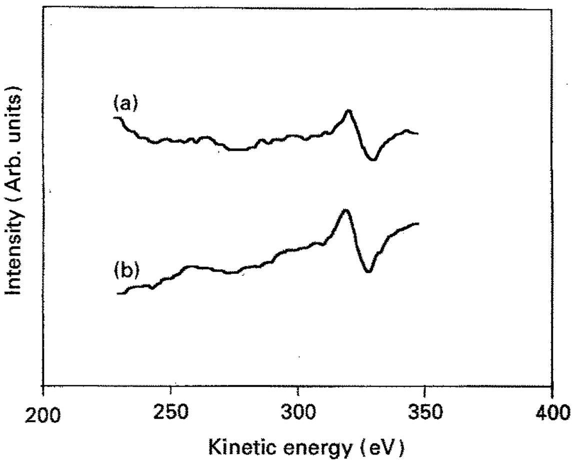

Figure 7 Auger electron spectra of the palladium on the aerogel surfaces, for (a) aerogel catalyst I, and (b) aerogel catalyst II.

vessels used in the supercritical drying, were detected during this measurement.

TABLE II The Knudsen diffusion coefficient, D_K, and effective diffusion coefficient, D_e, of methane at 500 °C of the palladium-supported alumina–silica aerogels

	D_K	D_e
Aerogel catalyst I	6.91×10^{-2}	$4.29 \times 10^{-2}/\tau_I$
Aerogel catalyst II	2.87×10^{-2}	$1.12 \times 10^{-2}/\tau_{II}$

TABLE III The dispersion of palladium in the alumina–silica aerogels as measured by CO adsorption

	Dispersion
Aerogel catalyst I	1.247
Aerogel catalyst II	0.325

4. Discussion

A large difference in the activity for methane combustion was observed between aerogel catalyst I and II (see Fig. 5). The causes for this difference in activity depend on the following factors. The first factor can be found in the aerogel supports. As shown in Fig. 6, the pore-size distributions of the aerogels are different, with both aerogel sizes in the meso-pore range [8]. Knudsen diffusion is dominant over this range. The coefficient of Knudsen diffusion, D_K ($m^2\,s^{-1}$), is given by the following equation [9, 10]

$$D_K = 3.067\,r(T/M_A)^{1/2} \qquad (1)$$

where r is the pore diameter, T the temperature (K), and M_A the molecular weight of the vapour.

The diffusion coefficients of methane for the aerogel catalysts at 500 °C were calculated using this equation and are listed in Table II. Moreover, the effective diffusion coefficient, D_E ($m^2\,s^{-1}$), is given by [9, 11]

$$D_E = \varepsilon_p D_K/\tau \qquad (2)$$

where ε_p is the pore volume fraction, and τ the tortuosity factor. The tortuosity factor, τ, is determined by the structure of the pores and difficult to calculate theoretically [9]. However, several researchers have recommended values of τ between 3 and 5 [11, 12]. The tortuosity factor for each catalyst is termed τ_I for catalyst I and τ_{II} for catalyst II. The effective diffusion coefficients, D_E, are also listed in Table II. τ_I and τ_{II} can be almost equal from the result of TEM (see Fig. 3). It should be noted that D_E of aerogel catalyst I can be more than several times larger than that of aerogel catalyst II.

The second factor can be found in the catalyst itself. From the results of the AES (Fig. 7), the electron states of the palladium particle surface are similar to each other. Another possible factor is dispersion of the palladium particles. The palladium dispersion was evaluated by the adsorption of carbon monoxide (CO), because CO is selectively adsorbed on the palladium surface [13]. The degree of palladium dispersion is evaluated by the following equation,

$$\text{Pd dispersion (\%)} = A_{CO} M_{Pd}/R\,W_{Pd} \times 100 \qquad (3)$$

where A_{CO} is the amount of CO adsorbed per 1 g sample ($ml\,g^{-1}$), M_{Pd} the atomic weight of palladium, R the gas constant ($ml\,mol^{-1}$), the W_{Pd} the weight of palladium per 1 g sample ($g\,g^{-1}$).

The results of the CO adsorption are given in Table III. The palladium dispersion of aerogel catalyst I is four times greater than that of aerogel catalyst II. This is attributed to the fact that some of the palladium in aerogel catalyst II surrounded by the alumina–silica support [2]. These factors concerning the support and catalyst influence the activity for methane combustion.

5. Conclusion

Palladium-supported alumina–silica aerogels are prepared by two different supercritical drying methods. The catalyst prepared in the autoclave exhibits more combustion activity than that prepared in the CO_2 extractor. This is attributed to the greater dispersion of palladium particles and the larger pore-size distribution of the aerogel support found in the aerogel dried in the autoclave.

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