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Sol-gel preparation and thermal stability of Pd/γ-Al_2O_3 catalysts

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A series of Pd/γ-Al_2O_3 catalysts with a designed loading of 1 wt % were prepared by the sol-gel method using boehmite (AlOOH) sols and various palladium compounds. These materials were developed for later use as inorganic membranes. The samples were calcined at 400 °C in flowing O_2 to decompose the Pd complex and change the phase of the support to γ-Al_2O_3. H_2 pulse chemisorption was used to determine the average Pd particle sizes, while particle size distributions were obtained from TEM micrographs. XRD was used to determine the crystallinity of the γ-Al_2O_3 support after extended treatments at 650 °C in O_2 and H_2 atmospheres. The physical properties of the support were studied using nitrogen adsorption-desorption at 77 K. Initial BET surface areas were about 350 m^2/g. Pore size distributions were very narrow and centered at 3.6 nm, but broadened and became bimodal during the 650 °C treatments. An ion-exchanged sample prepared by traditional methods was used as a basis for comparison to the sol-gel samples. © *1999 Kluwer Academic Publishers*

1. Introduction

Membrane reactors are becoming of interest to researchers because of their ability to accomplish reaction and separation in one step, especially in cases where the reaction is equilibrium-limited. The purpose of the membrane is to selectively remove one of the products, driving the reaction toward further conversion. A membrane reactor may also be applied to other situations, such as selective oxidation or hydrogenation, where the desired product is a reaction intermediate. A schematic of an example configuration is shown in Fig. 1. In this case, the membrane plays a different role and the reactants are fed on opposite sides of the membrane. For example, hydrogen has been permeated through a dense Pd-based membrane and reacted with acetylene [1] or phenol [2], giving a higher yield of the intermediate hydrogenation products. The membrane has a dual function: it controls the diffusion of hydrogen and also acts as a catalyst. However, dense Pd membranes are less mechanically and thermally stable compared to porous ceramic membranes. Dense Pd membranes are also less permeable although they are usually more selective to hydrogen. Recently, γ-Al_2O_3 mesoporous membranes have been modified with a film of Pd deposited by CVD [3] and nanoparticles of Pd have been deposited on a support by the sol-gel method [4, 5]. These types of membranes have the advantage of being mechanically more stable with higher permeabilities than dense membranes while maintaining a good selectivity to hydrogen.

The sol-gel method of preparing supported metal catalysts lends itself to the preparation of supported catalytic membranes. The method is unique in that the molecular precursor of the support material and the metal precursor are both present in the initial solution. A greater degree of control over the final catalyst properties can be achieved in comparison to traditional methods. Advantages include: (i) superior homogeneity and purity, (ii) well-defined pore size distributions, (iii) large surface areas, (iv) better microstructural control of supported metal particles, (v) improved thermal stability of the supported metals, (vi) the ease with which additional elements can be added, and (vii) the ability to use the starting sols to form inorganic membranes. To form a γ-Al_2O_3 membrane, a boehmite (AlOOH) sol is slip-cast onto a support material such as α-Al_2O_3. A gel layer is formed as the coating dries. Capillary pressure generated by the porous nature of the support draws the liquid of the sol through the support, leaving behind a layer of colloidal AlOOH particles. Different metal salts can be added to the sol to form a membrane with dispersed metal particles. The metal-containing membrane can be used simultaneously as a catalyst and a separator.

In this paper, the preparation and characterization of a series of Pd/γ-Al_2O_3 catalysts prepared from boehmite sols is reported. Information on the surface area, pore size, pore volume, and dispersion of Pd is discussed. The thermal stability of the support and the dispersed metal at 650 °C in oxidizing and reducing atmospheres

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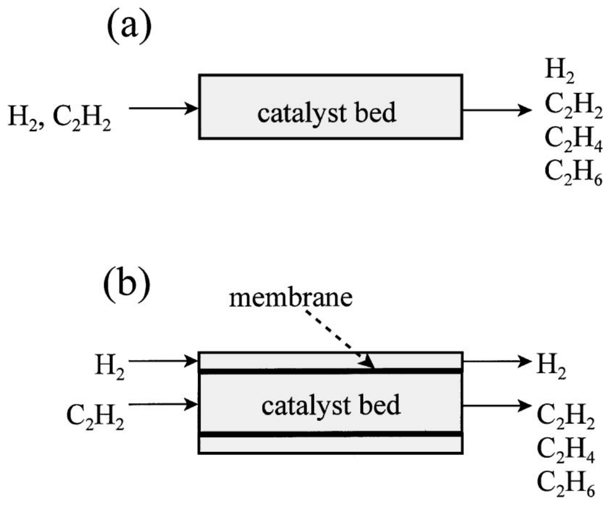

Figure 1 Schematic of (a) a conventional packed bed reactor and (b) a packed bed membrane reactor for the hydrogenation of acetylene.

is studied. Results from sintering experiments with sol-gel samples are compared to a sample prepared by the traditional method of ion exchange.

2. Experimental

2.1. Preparation of Pd/γ-Al_2O_3 catalysts

The γ-Al_2O_3 gels were formed using a sol-gel procedure based on the work of Yoldas [6]. In a typical synthesis, aluminum sec-butoxide was mixed with excess deionized water for 15 min at 85 °C, evolving butanol. The hydrolyzed product was peptized overnight at $T > 80\,^\circ C$ with dilute HCl in a closed container. The final molar ratios were $Al(OC_4H_9)_3$:H_2O:HCl = 1:100:0.07. This led to the formation of a clear, stable boehmite (AlOOH) sol. Pd was introduced to the sol by adding a designed amount of $(NH_4)_2PdCl_6$, $[Pd(NH_3)_4](NO_3)_2$ (both from Strem Chemicals, Newburyport, MA), or palladium(II) acetylacetonate (Alfa Aesar, Ward Hill, MA). The precursors were added directly to the sol with the exception of $Pd(acac)_2$, which was first dissolved in 10 ml of acetone because of its very low solubility in water. The sol was stirred in a closed container for 15 min to dissolve the metal precursor and then the container was opened and maintained at about 85 °C to form a gel through evaporation. The sample containing $Pd(acac)_2$ was stirred at 50 °C to avoid quick evaporation of the acetone and subsequent loss of solubility. The resulting gels were dried overnight in air at 110 °C.

An ion-exchanged sample was prepared by traditional methods. The compound $(NH_4)_2PdCl_6$ was used as the metal precursor and a commercial γ-Al_2O_3 (97.7% Al_2O_3, Strem Chemicals, Newburyport, MA) was used as the support material. A designed amount of the precursor was dissolved in deionized water and added to a slurry of the support. In order to maximize the adsorption of the complex, which is negatively charged when dissolved in water, the pH of the slurry was adjusted with HCl to a pH of about 3. This results in a positively charged γ-Al_2O_3 surface, since the pH is well below that of its point of zero charge (PZC = pH ~7–8). The slurry was stirred overnight at room temperature and then washed with deionized water. The filter cake was then dried in a vacuum desiccator.

2.2. Thermal analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed using an SDT 2960 Simultaneous DTA-TGA or a Hi-Res TGA 2950 Thermogravimetric Analyzer, both from TA Instruments. Platinum pans were used to hold the sample and the reference (α-alumina). The analysis was performed using flowing O_2 with a 10 °C/min temperature ramp. A Thermolab mass spectrometer, in series with the TGA, was used to determine the identity of the gases evolved from the sample.

2.3. Pretreatment and sintering

Prior to any characterization studies, the catalysts were calcined in flowing O_2 at 400 °C for 30 min followed by reduction in flowing H_2 at 400 °C for 1 h. Sintered samples were reduced in H_2 at 400 °C before chemisorption measurements were made. The pretreatment and dispersion measurements were performed using a pyrex microreactor to hold the sample, while the sintering studies were performed using a quartz microreactor. Pretreatment and sintering temperatures were obtained using a heating rate of 10 °C/min. This rate was controlled through the use of a temperature programmer. A gas flow rate of 30 ml/min was used in all of the pretreatment and sintering experiments. This flow rate was maintained through the use of Tylan mass flow controllers. During the experiments, a stream of inert gas such as argon was used to flush O_2 or H_2 from the microreactor. All gases were UHP grade, and the appropriate heaters and traps were used to maintain the integrity of the gas streams.

2.4. Surface area and pore size measurements

A Coulter Omnisorp Porosimeter was used to measure the surface area and pore size distribution of all the materials prepared. A 100 mg sample was placed in a pyrex holder, heated to 200 °C, and evacuated to 10^{-5} torr. The full adsorption-desorption isotherm was obtained at 77 K using UHP nitrogen as the adsorbing gas. Surface areas were calculated using the BET equation, and pore size distributions were obtained using the desorption isotherm.

2.5. Hydrogen chemisorption

Hydrogen chemisorption measurements of the palladium dispersion were performed using the dynamic pulse method, which has been described in detail elsewhere [7]. Weakly adsorbed hydrogen is not measured when this method is used. Approximately 200 mg of catalyst was placed in a pyrex microreactor and subjected to the standard pretreatment at 400 °C. The reactor was flushed with argon and rapidly cooled to 25 °C.

Small amounts of H_2 (85.8 μl) were pulsed through the reactor until saturation was attained. A gas chromatograph equipped with a thermal conductivity detector was used to monitor the volume of H_2 leaving the reactor following the addition of each pulse. The saturation point was determined when the integrated area from successive peaks was equal. The volume of hydrogen chemisorbed was used to calculate the dispersion (D_H), which is the percentage of metal atoms in surface sites.

2.6. Electron microscopy

A Phillips EM 410 or a Zeiss EM 10 transmission electron microscope equipped with either a tungsten or a LaB_6 filament was used to determine metal particle size distributions. The samples were prepared by sonicating 10 mg of catalyst in 10 ml of ethanol. One drop of the suspension was placed on a holey carbon copper grid and allowed to dry completely. Typical magnifications required were 185 or 300 k with an accelerating voltage of 100 keV. Photographs were enlarged to 8″ × 10″ size before measurement of particle sizes.

3. Results

3.1. Formation of γ-Al_2O_3 support

Thermal analysis was performed on boehmite powder prepared by the sol-gel method to pinpoint the temperature at which the phase transition to γ-Al_2O_3 occurred in an oxygen atmosphere. The weight loss and first derivative of the weight loss curve are shown in Fig. 2a, with a simultaneous DTA curve shown in Fig. 2b. The two weight loss peaks consisted of water released from the sample as identified by mass spectrometry. Also identified was the HCl used in the synthesis, which was lost between 300 and 400 °C. The second weight loss at 407 °C and the corresponding endotherm at 402 °C indicated the transition from AlOOH to γ-Al_2O_3. This was confirmed by X-ray diffraction of the boehmite powder after drying at 110 °C (AlOOH, Fig. 3a) and after calcination at 400 °C (γ-Al_2O_3, Fig. 3b). The sol-gel boehmite and γ-Al_2O_3 were poorly crystalline. The physical properties of the blank γ-Al_2O_3 support are shown in the first line of Table I.

3.2. Characterization of Pd/γ-Al_2O_3 catalysts with a designed metal loading of 1 wt%

The effect of the oxygen pretreatment on the dried Pd/AlOOH gels was studied using simultaneous TGA-mass spectrometry. All three Pd precursors decomposed between 300 and 400 °C, with HCl (the peptization agent) also being lost in this temperature range. The maxima in the weight losses corresponding to the phase transition of the supports occurred around 400 °C, the same as for the blank support sample. The physical characteristics of the 1.0 wt% Pd designed catalysts after pretreatment are shown in Table I. The sol-gel samples synthesized using different Pd precursors are designated SG-1, SG-2, and SG-3, and the ion-exchanged sample is designated IE-1. Metal loadings were determined by ICP analysis at Galbraith Laboratories (Knoxville, TN, USA). The actual metal loadings were all less than the designed amount of 1 wt%. The ion-exchanged sample had the lowest loading at

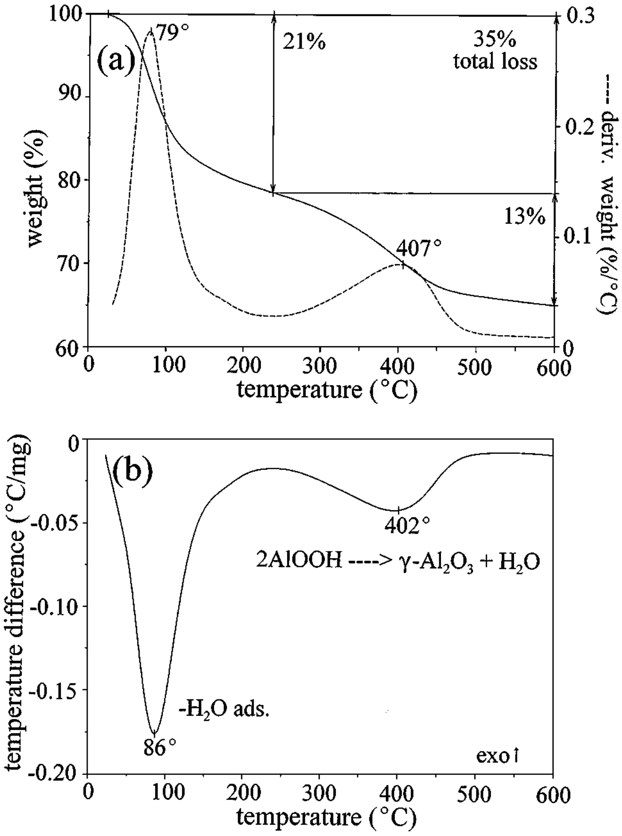

Figure 2 Weight loss (a) and temperature difference (b) curves for boehmite (AlOOH) powder prepared by the Yoldas method [6] and dried at 110 °C. Also shown in (a) is the first derivative of the weight loss curve. The experiment was performed in flowing O_2 at a ramp of 10 °C/min using α-Al_2O_3 powder as a reference.

TABLE I Pd/γ-Al_2O_3 catalyst properties

Sample	Pd precursor	Pd wt% des.	Pd wt% ICP	BET area (m^2/g)	Pore vol (ml/g)	Avg pore dia (nm)	D_H (%)[a]	d_m (nm)[b]
Blank	—	—	—	360	0.28	3.6	—	—
SG-1	$[Pd(NH_3)_4](NO_3)_2$	1.0	0.66	332	0.33	3.6	31	3.2
SG-2	$Pd(acac)_2$	1.0	0.73	361	0.30	3.6	36	2.7
SG-3	$(NH_4)_2PdCl_6$	1.0	0.70	352	0.39	3.6	20	4.9
IE-1	$(NH_4)_2PdCl_6$	1.0	0.59	172	0.48	8.5	41	2.4

[a] D_H is dispersion of Pd as measured by hydrogen chemisorption, $H : Pd_{(surface)} = 1 : 1$. This is a measure of the percentage of Pd atoms in surface sites.

[b] d_m is metal particle size, calculated by $98.2/D_H$ based on a cubic particle model with 5 faces exposed to the gas phase.

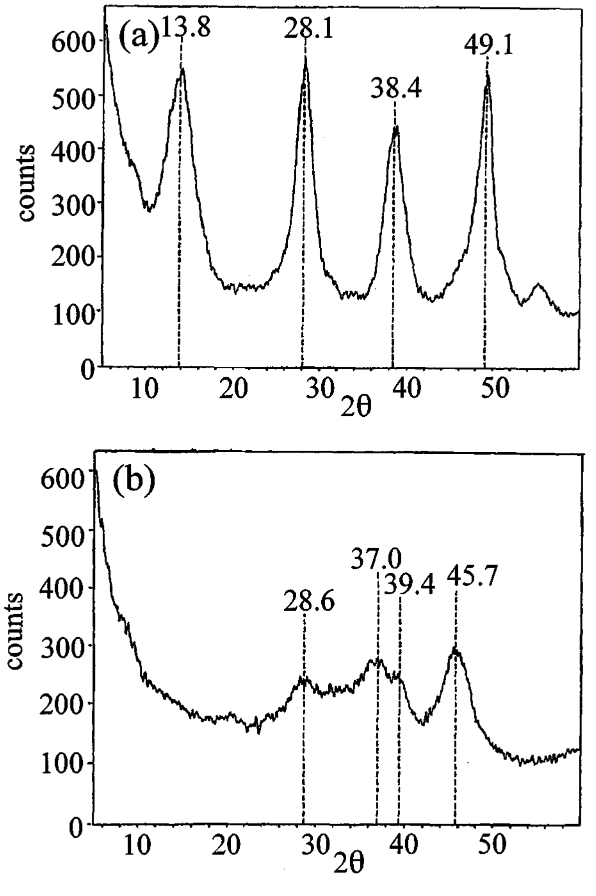

Figure 3 X-ray diffraction patterns for (a) AlOOH powder dried at 110 °C and (b) AlOOH powder calcined at 400 °C (γ-Al_2O_3).

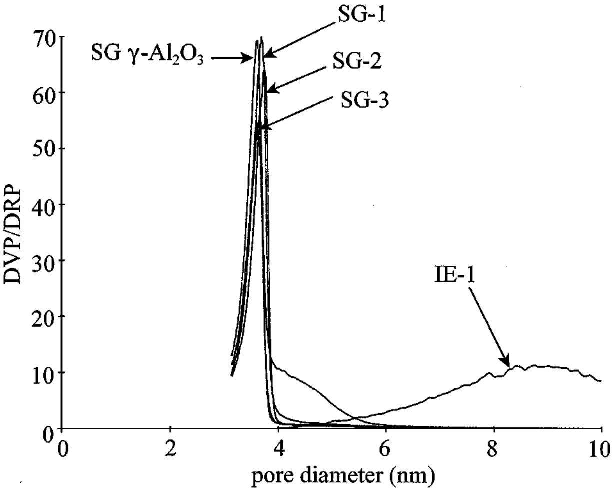

Figure 4 Pore size distributions for blank γ-Al_2O_3, sol-gel Pd/γ-Al_2O_3 (SG-1,-2,-3,), and ion-exchanged Pd/γ-Al_2O_3 (IE-1). All samples were pretreated at 400 °C. The y-axis (DVP/DRP) is the pore size distribution function, or the differential of the pore volume with respect to the pore radius.

0.59 wt% while SG-1, SG-2, and SG-3 had virtually identical loadings of about 0.7 wt%.

BET surface areas for the sol-gel samples were around 350 m^2/g with narrow pore size distributions centered at 3.6 nm, the same as for the blank γ-Al_2O_3 sample (Fig. 4). Pore volumes ranged from 0.3 to 0.4 ml/g. In contrast, the commercial support used for the ion-exchanged sample had a BET surface area of 172 m^2/g and a pore volume of 0.48 ml/g. This sample also had a very broad pore size distribution centered at around 9 nm (Fig. 4). Metal dispersions (D_H) measured by H_2 pulse chemisorption varied from 20 to 36% for the sol-gel samples. The highest dispersion occurred in the ion-exchanged sample at 41%. An estimate of the Pd particle size (d_m) was calculated from the dispersion measurement using a cubic particle model with 5 faces exposed to the gas phase. The value used for the Pd density at 25 °C was 11.40 g/ml, and the area of one Pd surface atom was taken to be 7.895 Å^2 [8]. The calculated average Pd particle size was larger than the size of the pore (3.6 nm) for SG-3.

3.3. Other sol-gel Pd/γ-Al_2O_3 catalysts

Shown in Table II are data from sol-gel Pd/γ-Al_2O_3 samples prepared with different metal loadings using $(NH_4)_2PdCl_6$ as the metal precursor (~ SG-3). The support properties are similar to the 1.0 wt% designed samples, and the dispersions are the same as for SG-3 except for the 0.3 wt% designed sample, which has a higher dispersion. An effort was made to prepare a 1.0 wt% sample with a higher dispersion than SG-3. The data for this sample are shown in Table III. For this sample (SG-7), the sol was stirred for 24 h at room temperature after the addition of the Pd precursor to maximize the adsorption of the precursor onto the colloidal boehmite particles. The actual metal loading is slightly higher than that for SG-3, as is the metal dispersion. Data collected from TEM, however, show that the average Pd particle size is almost equal.

TABLE II Samples prepared with different Pd metal loadings using $(NH_4)_2PdCl_6$ as the precursor

Sample	Pd wt% des.	Pd wt% ICP	BET area (m^2/g)	Pore vol (ml/g)	Avg pore dia (nm)	D_H (%)	d_m (nm) 98.2/D_H
SG-4	0.6	0.49	306	0.32	3.6	20	4.9
SG-5	0.4	0.33	324	0.36	3.6	21	4.7
SG-6	0.3	0.26	302	0.34	3.6	32	3.1

TABLE III Effect of sol stirring time on catalyst properties (1 wt% designed Pd, using $(NH_4)_2PdCl_6$)

Sample	Stir time (h)	Pd wt% ICP	BET area (m^2/g)	Pore vol (ml/g)	Avg pore dia (nm)	D_H (%)	d_m (nm) 98.2/D_H	d_m (nm) TEM
SG-3	1/4	0.70	352	0.39	3.6	20	4.9	2.2
SG-7	24	0.80	366	0.31	3.6	32	3.1	2.0

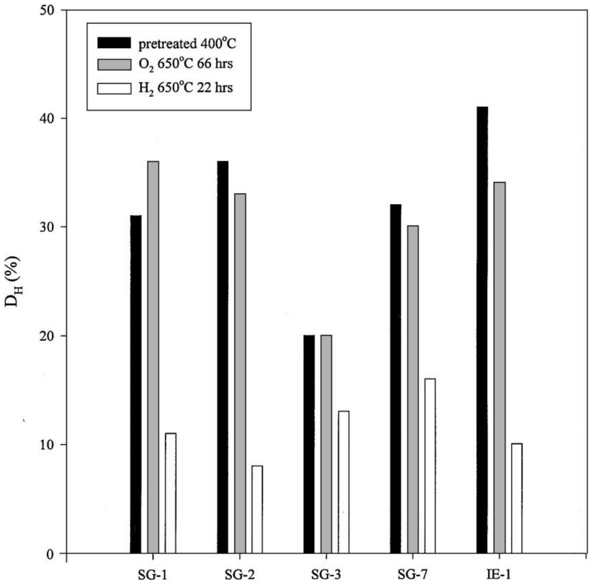

Figure 5 Dispersion of Pd (D_H) in Pd/γ-Al_2O_3 catalysts pretreated in O_2 and H_2 at 400 °C, sintered in O_2 at 650 °C for 66 h, and sintered in H_2 at 650 °C for 22 h. The dispersion is the percentage of metal atoms in surface sites.

3.4. Thermal stability of the dispersion of Pd

The stability of the dispersion of Pd for sol-gel and ion-exchanged samples was tested at 650 °C in O_2 and H_2 environments. This temperature was chosen because it is sufficiently high to affect the metal dispersion ($T > 500$ °C) [9] while not causing a phase change in the support. Fig. 5 shows the change in the dispersion with different atmospheres for the sol-gel and ion-exchanged samples. The time period of O_2 treatment was 66 h and for H_2 treatment it was 22 h. In general, the dispersion of Pd was stable in an oxygen atmosphere but unstable in a hydrogen atmosphere. The order of stability for the catalysts in flowing hydrogen was SG-3 > SG-7 > SG-1 > SG-2 ≅ IE-1. SG-3 was the most stable with a 35% decrease in dispersion. IE-1 had the highest initial dispersion and the largest pore size, resulting in the least stable catalyst with a 76% loss in dispersion. SG-2, which was made with an organometallic precursor, Pd(acac)$_2$, had a similar stability to IE-1.

Particle size distributions were calculated for sol-gel sample (SG-3) and the ion-exchanged sample (IE-1). The distributions before and after sintering in H_2 are shown in Fig. 6a and b. The distribution for both samples shifts to higher particle size following the sintering treatment. Particles as large as 7 nm for the sol-gel sample and 13 nm for the ion-exchanged sample were apparent in the micrographs. The initial particle size distribution for IE-1 is much narrower than that observed for the sol-gel sample, with a majority of the particles between 1 and 2 nm. However, after sintering in hydrogen, the distribution broadens to a much greater extent.

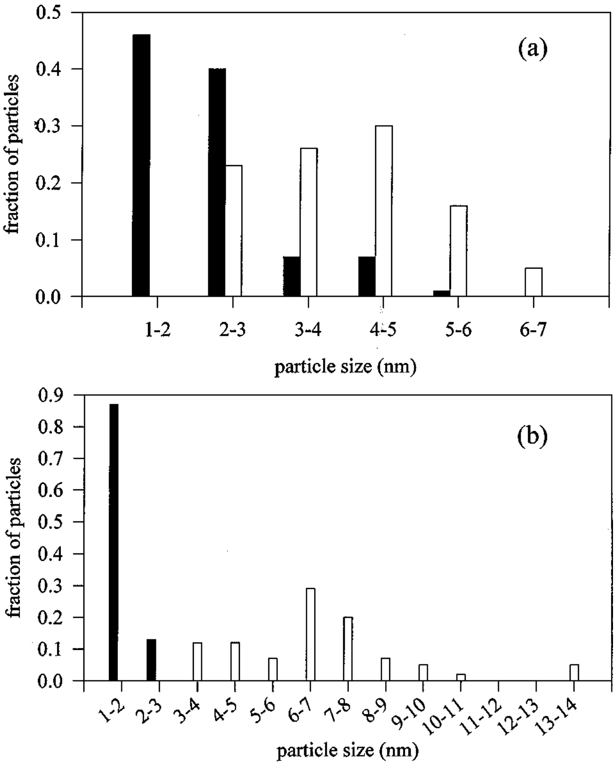

Figure 6 Particle size distributions obtained by TEM for (a) SG-3 and (b) IE-1 before (■) and after (□) treatment in flowing H_2 at 650 °C for 22 h.

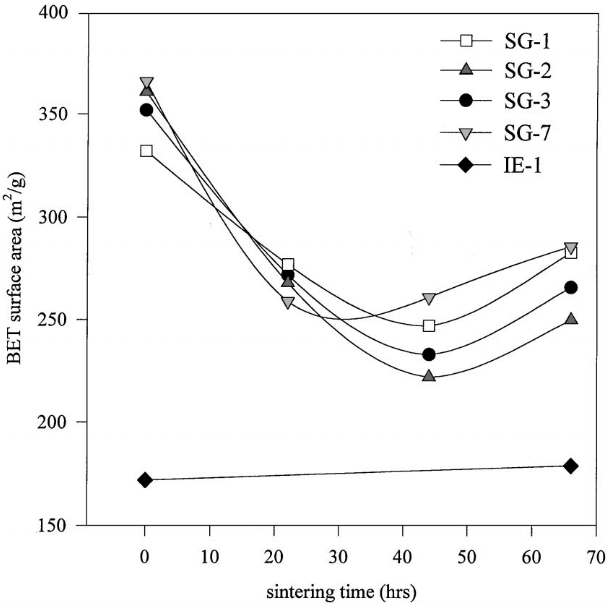

Figure 7 Effect of sintering time on the BET surface area of Pd/γ-Al_2O_3 in flowing O_2 at 650 °C.

3.5. Stability of sol-gel γ-Al_2O_3 supports

The effect of the 650 °C treatments in oxygen and hydrogen on the properties of the γ-Al_2O_3 supports was studied. The BET surface area of blank γ-Al_2O_3 in flowing H_2 or O_2 dropped from 360 to 250 m^2/g (31% loss), independent of atmosphere. Fig. 7 shows the effect of sintering time on the surface area of the Pd/γ-Al_2O_3 catalysts in flowing O_2. The BET surface area dropped about 15–30% for the sol-gel samples, while the surface area of IE-1 (commercial γ-Al_2O_3 support) remained approximately the same. In Fig. 8, the effect of sintering time on the catalyst pore volume in flowing O_2 is shown. The ion-exchanged sample showed a slight increase in pore volume after 66 h of treatment,

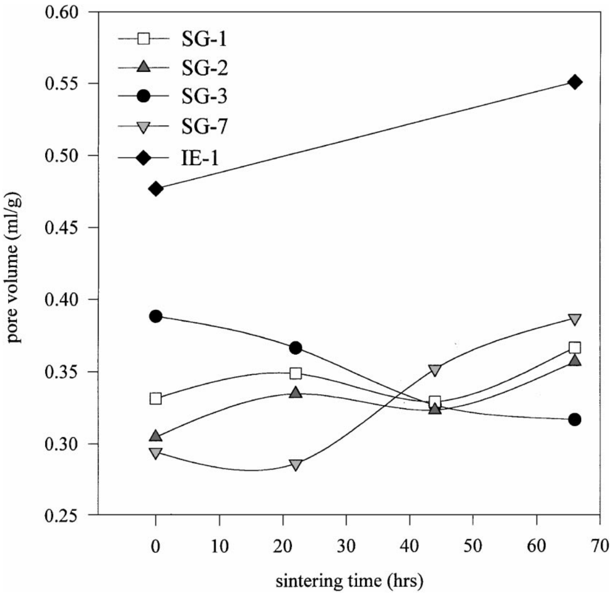

Figure 8 Effect of sintering time on the pore volume of Pd/γ-Al_2O_3 in flowing O_2 at 650 °C.

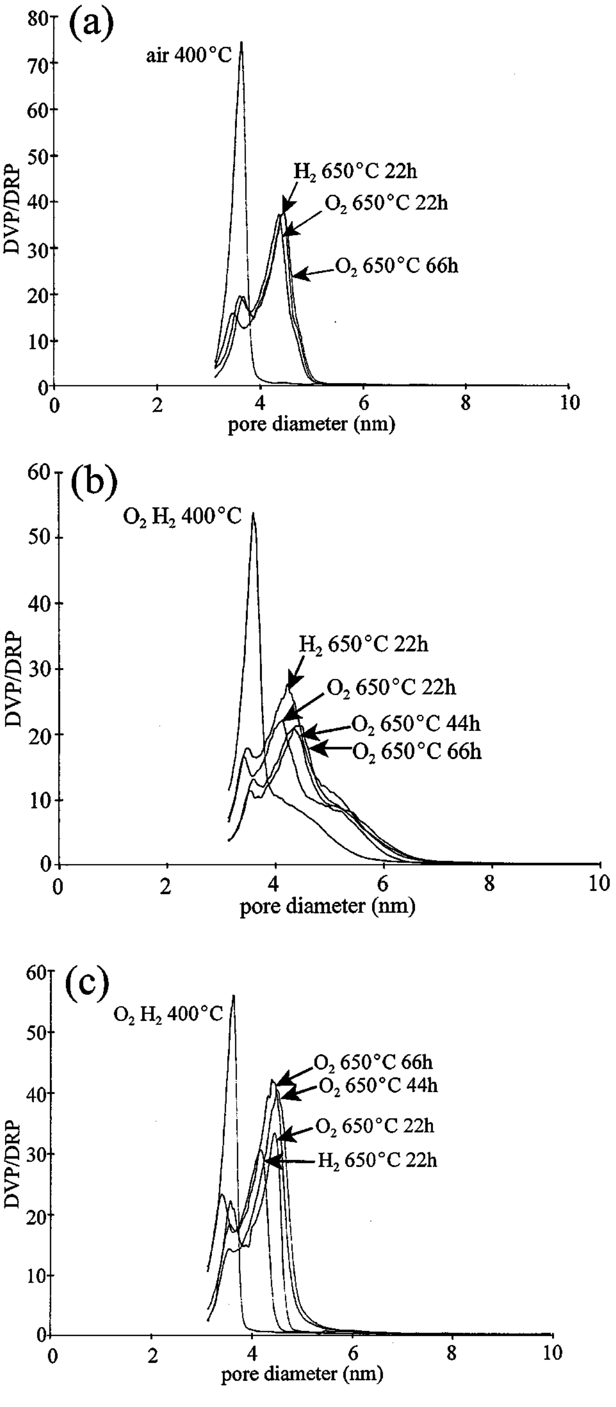

Figure 9 Effect of sintering time and atmosphere on the pore size distributions of (a) blank γ-Al_2O_3, (b) SG-3 Pd/γ-Al_2O_3, and (c) SG-7 Pd/γ-Al_2O_3. The y-axis (DVP/DRP) is the pore size distribution function, or the differential of the pore volume with respect to the pore radius.

while the pore volumes of the sol-gel samples are all roughly within the same range of 0.28 to 0.39 ml/g before and after 66 h.

The pore size distributions of blank γ-Al_2O_3 before and after sintering treatments in O_2 and H_2 are shown in Fig. 9a. The initial distribution of the sample calcined at 400 °C became broader and bimodal after treatment at 650 °C. The change in pore size was independent of atmosphere or time. In Fig. 9b and c, the distributions for SG-3 and SG-7 are shown. The effect of the heat treatment on the pore size distributions is similar as for the blank γ-Al_2O_3 sample, shifting to a new maximum at 4.5 nm.

Powder X-ray diffraction (XRD) was performed on the SG-3 sample to determine if any further phase changes were taking place during the 650 °C treatments. Fig. 10a shows the XRD pattern for SG-3 after pretreatment at 400 °C. This pattern matches that of the blank γ-Al_2O_3 sample shown in Fig. 3b. After treatment in H_2 for 22 h (Fig. 10b) and O_2 for 66 h (Fig. 10c), the patterns show a slight increase in crystallinity but the support is still γ-Al_2O_3.

4. Discussion

In 1964, Lippens and de Boer [10], using XRD, found that alumina went through several transition stages depending upon the temperature: crystalline AlOOH $\xrightarrow{450\,^\circ\mathrm{C}}$ γ-Al_2O_3 $\xrightarrow{850\,^\circ\mathrm{C}}$ δ-Al_2O_3 $\xrightarrow{1000\,^\circ\mathrm{C}}$ θ- + α-Al_2O_3 $\xrightarrow{1200\,^\circ\mathrm{C}}$ α-Al_2O_3. It was noted that poorly crystalline AlOOH could convert to γ-Al_2O_3 at temperatures as low as 350 °C. Features that make γ-Al_2O_3 attractive as a catalyst support are high surface area, well-defined pore size distribution, and stability in a wide temperature range. The γ-Al_2O_3 material prepared in this study from AlOOH sols also has a small pore diameter (3.6 nm), which makes it attractive for membrane coatings. Aging of γ-Al_2O_3 at 600–700 °C typically gives a loss in surface area of around 30% [11–13]. The average pore size remains almost constant until about 1000 °C, when the pore size increases dramatically during the onset of the phase change to α-Al_2O_3 [13–15]. For the sol-gel γ-Al_2O_3 supports prepared in this study, aging at 650 °C in O_2 for 66 h resulted in a similar loss in surface area (20–30%). The primary maximum of the pore size distribution shifted to about 4.5 nm. However, a small portion of the pores remained at 3.6 nm, resulting in a secondary maximum. In another study of the aging of amorphous boehmite [16], the pore size distribution for a sample that was calcined at 800 °C had a primary maximum at 6.0 nm with two secondary maxima at 3.6 and 8.0 nm. As the temperature was increased, the

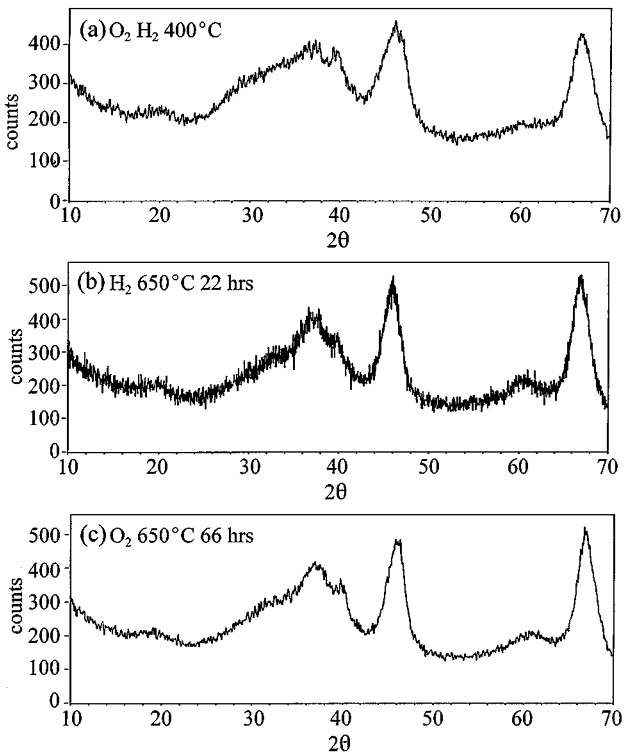

Figure 10 X-ray diffraction patterns of sol-gel Pd/γ-Al_2O_3 (SG-3) after (a) pretreatment in O_2 and H_2 at 400 °C, (b) sintering in H_2 at 650 °C for 22 h, and (c) sintering in O_2 at 650 °C for 66 h.

pore diameter continued to increase until 1200 °C, at which temperature there was a single broad maximum (α-Al_2O_3). Therefore, a bimodal or multimodal pore size distribution is indicative of a material in transition between phases.

Another interesting characteristic of the sol-gel materials is the minimum in surface area that occurs at 44 h for the supports aged in O_2 as shown in Fig. 7. The initial loss in surface area after 22 h of aging can be explained by a significant decrease in the total number of pores (Fig. 9b and c) caused by the further reaction of alumina species to form a more condensed gel structure. The maximum pore size shifts to a higher value due to merging of smaller pores. With further aging, the number of pores continues to decrease and the surface area decreases. After 66 h of aging, there is a slight increase in the surface area that is consistent for all of the sol-gel samples. This can be explained by an increase in the number of pores accessible to N_2. Some of the pores may have become closed due to the condensation reaction that are opened because of the extended heat treatment.

While the thermal stability of the support did not depend on atmosphere, the dispersion of Pd was stable in oxygen but not in hydrogen. This behavior was similar to a previous study on the thermal stability of Pd/SiO_2 prepared by the sol-gel method [17]. The catalysts in that study experienced about a 50% loss in dispersion after 22 h at 650 °C in flowing H_2 but did not sinter in flowing O_2 under the same conditions. At 650 °C, the sintering species in O_2 is PdO and the sintering species in H_2 is Pd metal. This leads to different thermal behaviors of the supported metal particles. Using electron microscopy, Chen and Ruckenstein have studied the behavior of Pd supported on γ-Al_2O_3 films [9, 18]. In flowing O_2, PdO was formed at 350 °C and small crystallites began to spread across the substrate [18]. By 500 °C, extensive spreading of all crystallites was observed. This phenomenon was also observed by other workers using controlled atmosphere electron microscopy (CAEM) on similar samples [19], and it was noted that at 650 °C no individual particles could be detected. This behavior is very different from Pd crystallites sintered in flowing H_2, in which only elemental Pd is present [9]. It was observed that no sintering occurred up to 500 °C, and when the sample was held at 650 °C, the bulk of the sintering took place within the first hour of treatment. Crystallite migration and coalescence were observed on a global scale, leading to a new particle size distribution. After 1 h, the sintering rate slowed down, involving only a few neighboring crystallites. It is important to note that the Tammann temperature (T_{melting} (K)/2) of Pd is about 640 °C, and the diffusion of metal particles above this temperature is enhanced [20].

Since the electron microscopy experiments discussed above were performed on planar substrates, the sintering behavior of Pd in a H_2 atmosphere may differ when the support is a porous three-dimensional solid as in this study. The pores could act as "chemical traps," and slow down the diffusion of particles as their size reaches the size of the pore [21]. Evidence for this phenomenon is shown in the comparison of particle size distributions for sol-gel and ion-exchanged Pd/γ-Al_2O_3 samples. Although the distribution for the ion-exchanged sample is much narrower prior to the sintering treatment, it broadens to a much greater extent than for the sol-gel sample. Similar results have been found for Pd/SiO_2 in a H_2 atmosphere [17] and for Rh/SiO_2 in an O_2 atmosphere [22]. The porous structure of catalysts prepared by the sol-gel method results in a greater retention of the metal dispersion during heat treatments at 650 °C.

The porous structure also allows for the sol-gel materials to be useful as membranes with catalytic properties. Blank γ-Al_2O_3 membranes prepared by sol-gel usually have a pore size of about 4 nm and the diffusion of gases through the membrane is governed by a Knudsen diffusion mechanism [23]. In a recent study of γ-Al_2O_3 membranes with dispersed metals (Ru, Rh, Pd, Ni, and Pt), the separation factor for a hydrogen/nitrogen mixture exceeded the value expected from Knudsen diffusion [24]. The permeation of hydrogen was promoted by the presence of the metal. If the pores are too small, as in the case of a microporous SiO_2 membrane, pore blockage by the supported metal particles can occur, resulting in the formation of defects [25]. Therefore, a useful catalytic membrane must have small enough pores to achieve separation of gases while maintaining a high dispersion of metal to avoid pore-plugging. The Pd/γ-Al_2O_3 materials prepared in this study have the potential to meet these criteria.

5. Conclusions

The following conclusions emerge from this study: (i) the sol-gel method is useful for preparing highly dispersed Pd/γ-Al_2O_3 catalysts with high surface areas and narrow pore size distributions, (ii) during heat treatment at 650 °C, the sol-gel γ-Al_2O_3 support loses about one-third of its surface area, and the average pore size increases while a small portion of the pores remain the original size, (iv) the growth of Pd particles in an oxygen atmosphere is very low due to the stability of PdO at the sintering temperature used in this study, (v) the dispersion of Pd in a hydrogen atmosphere at 650 °C decreases dramatically, forming a new particle size distribution, and (vi) the amount of sintering experienced by a Pd/γ-Al_2O_3 catalysts prepared by the sol-gel method is less than that of a catalyst prepared by the traditional method of ion-exchange due to the well-defined pore structure.

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