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Activity and selectivity of a Pd/γ-Al_2O_3 catalytic membrane in the partial hydrogenation reactions of acetylene and 1,3-butadiene

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A Pd/γ-Al_2O_3 membrane supported on a macroporous α-Al_2O_3 tube was prepared by sol–gel processing and used in the partial hydrogenation of acetylene and 1,3-butadiene. The average pore diameter of the Pd/γ-Al_2O_3 membrane was 3.6 nm. The gases were separated by Knudsen diffusion. The activity and selectivity of the Pd/γ-Al_2O_3 membrane was compared to that of Pd/γ-Al_2O_3 catalysts used in a conventional packed bed reactor. The highest selectivity to the partially hydrogenated products occurred when the reactant was premixed with H_2 and was passed through the membrane wall.

Keywords: Pd/γ-Al_2O_3, inorganic membrane, catalytic membrane reactor, acetylene hydrogenation catalyst, 1,3-butadiene hydrogenation catalyst

1. Introduction

In recent years, there have been several investigations of the use of membrane reactors in hydrogenation reactions [1]. Membranes are usually classified as dense (metal) or porous (metal or ceramic), and the reactant is fed on one side of the membrane, while hydrogen is fed on the opposite side and diffuses through the membrane. Dense membranes are permeable only to hydrogen, but can embrittle and must be extremely thin (1 μm) to have sufficient permeability to compete with porous membranes [2]. Several researchers have investigated the use of membrane reactors for partial hydrogenation reactions. Dense metal membranes have been studied for the partial hydrogenation of acetylene at 100 °C. These include a Pd/Ni membrane [3] and Pd, Pd/Ni, Pd/Ru, and Pd/Ag membranes [4]. Both studies found that the permeate hydrogen was very active and ethylene was the main product. Also of interest is the addition of hydrogen to one double bond of a diene. The selective hydrogenation of butadiene in crude 1-butene was performed using a catalytic hollow fiber membrane reactor at 40 °C [5]. The catalyst consisted of polymer-anchored palladium on the inside wall of cellulose acetate or polysulfone fibers and a selectivity of nearly 100% to 1-butene under mild reaction conditions.

Of particular interest is the use of highly dispersed metals supported on inorganic oxide membranes. This type of membrane offers a higher permeability and thermal stability than dense metal membranes while still combining separative and catalytic properties. It also has several advantages over a packed bed/inert membrane system. These include no catalyst loss, because the catalyst is contained in the membrane. Additionally, there is no pressure drop down the reactor, because there is no packed bed of catalyst. Metal oxide membranes are prepared by dipping a porous substrate into a solution of colloidal particles of the metal oxide or a precursor to the metal oxide [6]. The particles are concentrated on the substrate surface due to capillary forces and form a gel layer. A catalytic membrane can be formed by adding a water-soluble compound of the active metal to the sol [7]. The metal precursor is decomposed later during calcination of the membrane.

Metals that have a high activity for hydrogenation reactions include Rh, Ru, Pd, Pt and Ni [8]. However, Pd is unique in its ability to selectively hydrogenate alkynes and dienes in the presence of alkenes [9–11]. Acetylene and 1,3-butadiene are more strongly adsorbed on the metal surface than the alkene products. This effect results in an enhancement in the selectivity of the catalyst [9]. In an industrial reactor, the catalyst is usually a Pd/α-Al_2O_3 prepared by impregnating a low surface area ($\sim$20 m^2/g) support with a low loading of Pd ($\sim$0.04 wt%) [12]. The feedstock is made up of a small amount of the alkyne or diene in a large excess of the alkene and a Pd catalyst with low dispersion and low loading is required to inhibit the formation of the saturated product [13].

In this study, the feed stream had only the alkyne or diene present and required a higher metal loading and dispersion to achieve a complete conversion. The activity and selectivity of a sol–gel Pd/γ-Al_2O_3 membrane in the partial hydrogenation of acetylene and 1,3-butadiene were compared to the activity and selectivity of Pd/γ-Al_2O_3 powdered catalysts prepared by sol–gel and by the traditional method of ion-exchanging a Pd salt onto a commercial support. The powdered catalysts were used in a traditional reaction system in which the hydrogen is premixed with the reactant. The membrane was also tested in the pre-

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mixed mode. The physical properties of the materials are compared as well as the flux rates of pure gases through the Pd/γ-Al_2O_3 membrane and a SiO_2/γ-Al_2O_3 membrane also prepared by the sol–gel method.

2. Experimental

2.1. Preparation of the AlOOH, PVA/AlOOH and Pd/AlOOH sols

A Pd/AlOOH was used as the dipping solution for the formation of the Pd/γ-Al_2O_3 membrane. The preparation of the boehmite (AlOOH) sol was based on a method developed by Yoldas [14] and was used as the precursor to γ-Al_2O_3. Aluminum *sec*-butoxide (Strem Chemicals, Newburyport, MA) was added to deionized water at 85 °C and mixed for 15 min in an open container to evolve butanol. Dilute HCl was then added as a peptization agent. The final molar ratios were $Al(OC_4H_9)_3 : H_2O : HCl = 1 : 100 : 0.07$. The resulting solution was stirred overnight at 85 °C in a closed container to form a clear, stable sol of AlOOH particles. During the drying stage of membrane formation, there is a tendency for the gel layer to crack due to capillary forces. The binder polyvinyl alcohol (PVA) was used to retard this phenomenon, and the effects of the binder on the membrane structure have been previously reported [15]. The binder was added to the deionized water at 85 °C during the initial stage of the synthesis, and the amount used was designed to be 2 wt% of the total solution.

The preparation of boehmite sols containing Pd is fully described in a previous study [16]. Pd was introduced to the stable sol by adding a designed amount of $(NH_4)_2PdCl_6$ (Strem Chemicals, Newburyport, MA). The sol was stirred in a closed container at room temperature for 24 h to fully dissolve the metal precursor. Small portions of the AlOOH, PVA/AlOOH and Pd/AlOOH solutions were heated to 95 °C in order to evaporate the solvent and form gels. The gels were dried overnight in air at 110 °C and later calcined in flowing O_2. These samples were used to determine the physical characteristics of the membranes that could not be measured directly, such as surface area, pore size distribution, dispersion, and metal loading.

2.2. Preparation of supported membranes

An α-Al_2O_3 tube, purchased from US Filter, was used as a support for the membranes. The tube was sold under the name Membralox and was cut using a diamond blade into sections approximately 4 cm in length. A schematic of the structure of the tube with the sol–gel layer is shown in figure 1. The outer diameter of the tube was 10 mm and the inner diameter was 7 mm. The tube was dipped in the sol with the outer surface covered by a polyethylene film so that only the inner surface was in contact with the sol. The dipping time was 10 s. Between each dipcoat, the tube was allowed to dry for 24 h at room temperature, then calcined in a furnace using a 1 °C/min ramp. The blank AlOOH gel and the Pd/AlOOH membrane were calcined to a final temperature of 400 °C, while the membrane containing PVA was calcined up to a final temperature of 515 °C for complete removal of the binder. The final temperature was maintained for 3 h.

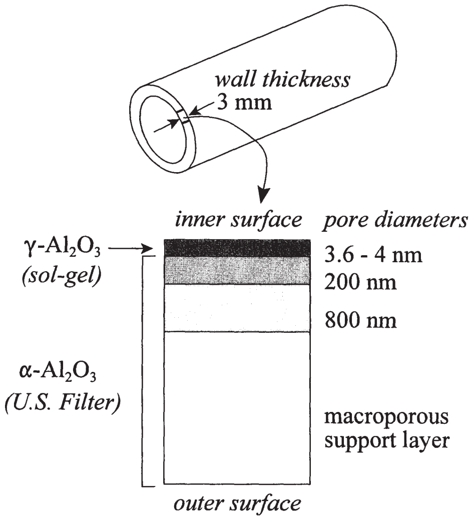

Figure 1. Configuration of sol–gel membrane supported on a macroporous α-Al_2O_3 tube (Membralox, US Filter). The average pore diameters of the α-Al_2O_3 and γ-Al_2O_3 layers are shown.

A SiO_2 toplayer was later added to the (PVA)/γ-Al_2O_3 membrane to repair any defects and further reduce the pore size. A silica sol was prepared at 80 °C using tetraethoxysilane (TEOS) and an excess of water (mol H_2O/mol Si $=$ 100). The pH was adjust to a value of 2 using dilute HCl. PVA was added in an amount required to form a 2 wt% solution. The tube supporting the (PVA)/γ-Al_2O_3 membrane was dipped in the silica sol so that the sol was only in contact with the inner surface of the tube. The dipping time was 30 s and the tube was dipped twice. Between each dipcoat, the tube was allowed to dry at room temperature for 24 h, then calcined at 1 °C/min up to a final temperature of 510 °C. The final temperature was maintained for 30 min.

2.3. Membrane reactor assembly

A schematic of the membrane reactor is shown in figure 2. The reactor body consisted of a stainless-steel outer shell through which gas could be passed. Within the outer shell was an inner shell made of stainless-steel tubing, glass, and the alumina membrane, which was connected to the glass tubing with a high-temperature ceramic adhesive (Resbond^{TM}, Cotronics Corp., Brooklyn, NY). The adhesive was also used to seal the ends of the alumina tube. The glass tubing was connected to the stainless-steel tubing using compression fittings and Viton o-rings. A thermocouple was placed down the center of the reactor and the tip was located midway down the alumina tube. A pressure gauge was located at the reactant inlet and both tube and shell outlets were vented to a fume hood. A heating tape

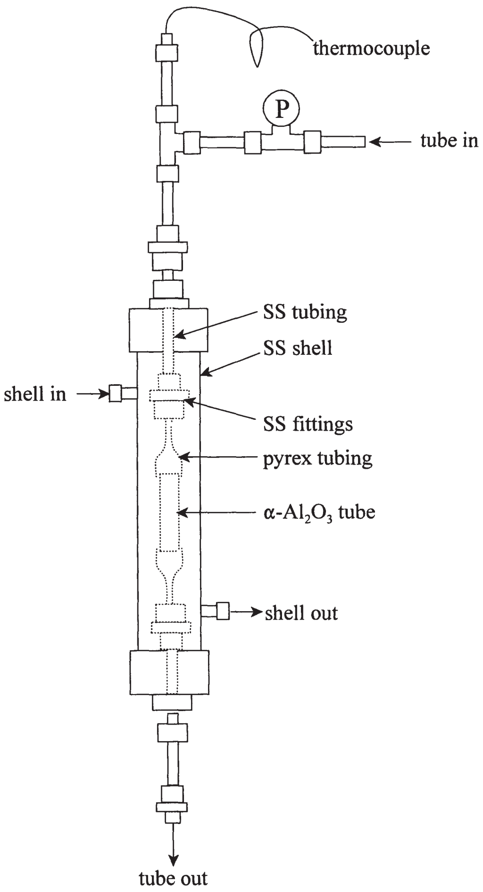

Figure 2. Schematic of the membrane reactor.

placed on the outside of the stainless-steel shell was used to heat the reactor and the temperature was controlled using a temperature programmer.

2.4. Preparation of Pd/γ-Al_2O_3 catalysts

Sol–gel Pd/γ-Al_2O_3 catalysts were prepared from Pd/AlOOH solutions. The entire solution was heated to 95 °C to form a gel, which was dried overnight at 110 °C. An ion-exchanged Pd/γ-Al_2O_3 sample was prepared by traditional methods and is described in a previous study [16]. The compound $(NH_4)_2PdCl_6$ was dissolved in a slurry at a pH of 3.0 together with a commercial γ-Al_2O_3 (97.7% Al_2O_3, Strem Chemicals, Newburyport, MA). The slurry was stirred overnight at room temperature and then washed with deionized water. The filter cake was then dried in a vacuum desiccator.

2.5. Pretreatment and chemisorption procedure

Prior to any characterization or reaction 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. The pretreatment procedure was performed using a pyrex microreactor to hold the sample. The Pd/γ-Al_2O_3 membrane was also reduced in H_2 for 1 h at 400 °C prior to reaction. The pretreatment temperature was obtained using a heating rate of 10 °C/min, which was controlled through the use of a temperature programmer. A gas flow rate of 30 ml/min was maintained using Tylan mass flow controllers. A stream of inert gas such as argon or helium was used to flush O_2 or H_2 from the reactor. All gases were UHP grade, and the appropriate heaters and traps were used to maintain the integrity of the gas streams.

Hydrogen chemisorption measurements of the dispersion of Pd were performed using the dynamic pulse method, which has been described in detail elsewhere [17]. 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. 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.

2.7. Flux measurements

The flow rates of pure gases at different pressures through the membranes were measured using the apparatus shown in figure 3. The shell inlet and the tube outlet were capped off so that the gas was forced through the membrane wall. The gas flow rate was controlled with Tylan mass flow controllers and measured with a bubblemeter. To calculate the flux, the gas flow rate was divided by the differential pressure across the membrane and the surface area of the membrane.

2.8. Reaction testing

The hydrogenation activity of the Pd/γ-Al_2O_3 catalysts and membrane were tested using either a 10% acetylene/Ar mixture or a 10% 1,3-butadiene/Ar mixture (UHP grade) as the reactant stream. For testing with a conventional reaction system, about 200 mg of catalyst was loaded into a pyrex microreactor, and the catalyst was pretreated using the standard procedure described in section 2.5. The reactor was cooled to the desired temperature and the reactant

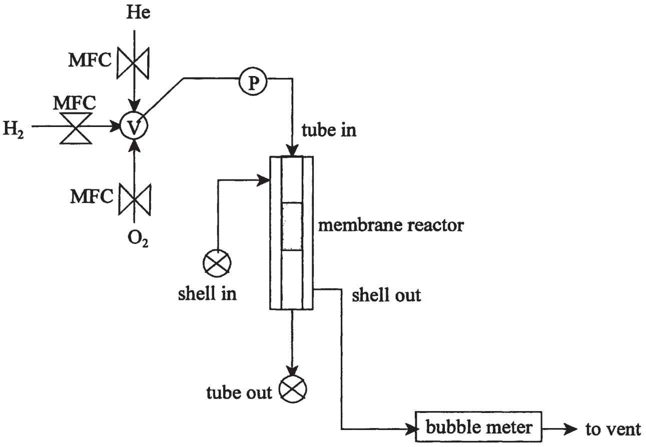

Figure 3. Design of apparatus for permeability experiment with pure gases (MFC = mass-flow controller, V = switching valve, P = pressure gauge).

stream was premixed with a controlled amount of hydrogen prior to entering the reactor. Pulses of the product gas were sent to a gas chromatograph equipped with a flame ionization detector and the gas flow rate was measured with a bubblemeter. When the Pd/γ-Al_2O_3 membrane reactor was used, the membrane was pretreated by the standard procedure, then cooled to the appropriate temperature. The reactant gas was passed through the tube inlet and H_2 was passed through the shell inlet. Argon was sometimes used to dilute the H_2 stream. Pulses of the tube outlet gas were sent to the gas chromatograph, and the flow rates of both outlet streams were measured with a bubblemeter. In the premixed mode, H_2 was added to the reactant stream and fed into the tube inlet. The shell inlet and tube outlet were closed so that the gas was forced through the membrane wall and exited through the shell outlet, similar to the permeability testing configuration shown in figure 3.

The results from the reaction tests are reported in terms of overall conversion of reactant and selectivity to the partially hydrogenated product. The selectivities are defined as follows:

$$S_{\text{ethylene}} = (\text{ethylene})/(\text{ethylene} + \text{ethane}),$$
$$S_{\text{butenes}} = (t\text{-2-butene} + \text{1-butene} + c\text{-2-butene})/(\text{butenes} + \text{butane}).$$

3. Results and discussion

3.1. Physical properties of membrane materials and catalysts

The results of the surface area, pore size and pore volume measurements of the γ-Al_2O_3, (PVA)/γ-Al_2O_3 and Pd/γ-Al_2O_3 gels are shown in table 1. The material prepared with PVA was calcined at 515 °C while the other two samples were calcined at 400 °C. The blank gel had a slightly higher BET surface area than the other two samples with additives. The pore size distributions of the these samples are shown in figure 4. The distribution for blank γ-Al_2O_3 was somewhat narrower than for the other two samples, and the average pore diameter of the (PVA)/γ-Al_2O_3 gel was slightly larger. The addition of the Pd compound did not affect the average pore diameter of that gel.

Table 1
Physical characteristics of membrane materials.

Material	BET area (m^2/g)	Avg. pore diam. (nm)	Pore vol. (ml/g)	Thickness[a] (μm)
γ-Al_2O_3 gel	360	3.6	0.28	–
(PVA)/γ-Al_2O_3	352	4.0	0.49	9.3
Pd/γ-Al_2O_3	334	3.6	0.37	11.0

[a] Thickness calculated assuming a homogeneous gel layer with density = 2.8 cm^3/g.

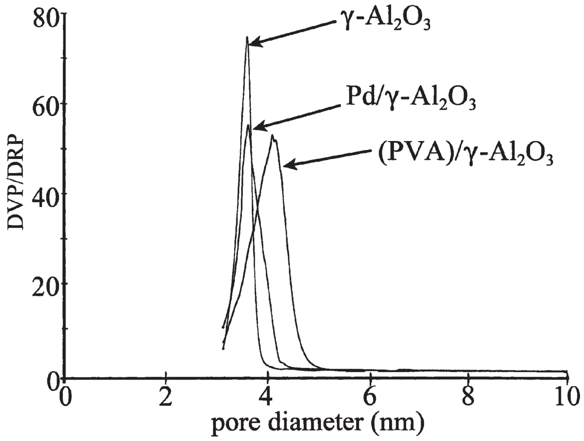

Figure 4. Pore size distributions for γ-Al_2O_3 gel, Pd/γ-Al_2O_3 membrane material, and (PVA)/γ-Al_2O_3 membrane material.

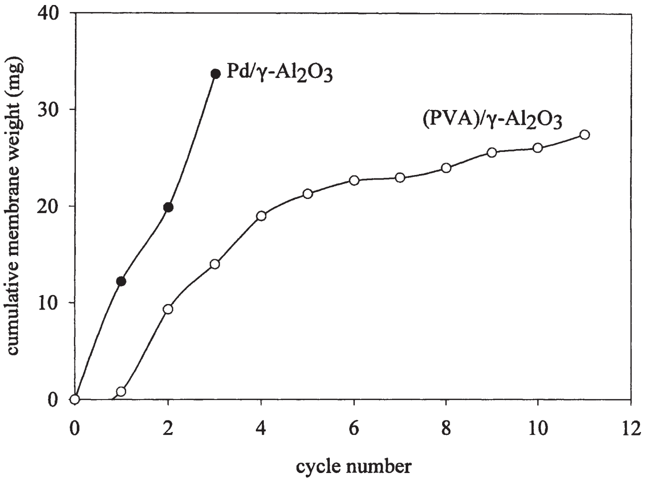

Figure 5. Cumulative membrane weight with successive dipping/drying/calcining cycles for Pd/γ-Al_2O_3 (●) and (PVA)/γ-Al_2O_3 (○) membranes supported on α-Al_2O_3.

The alumina tubes were weighed after each cycle of dip-coating/drying/calcining steps. The cumulative weight gain curves for the (PVA)/γ-Al_2O_3 and Pd/γ-Al_2O_3 membranes are shown in figure 5. The amount of weight gained in each cycle was much lower for the PVA/AlOOH solution

Table 2
Physical characteristics of Pd/γ-Al$_2$O$_3$ materials.

Material	BET area (m^2/g)	Avg. pore diam. (nm)	Pore vol. (ml/g)	Pd (wt%)	D_H[a] (%)	d_m[b] (nm)
SG[c]	366	3.6	0.31	0.80	32	3.1
IE	172	8.5	0.48	0.59	41	2.4
MEM	334	3.6	0.37	0.72	29	3.4

[a] Dispersion as measured by hydrogen chemisorption, $\mathrm{H:Pd_{surface}} = 1:1$.

[b] Metal particle diameter ($98.2/D_H$), assuming Pd density = 11.40 g/cm^3 and area of one Pd surface atom = 7.895 Å [18].

[c] SG = sol–gel-prepared catalyst, IE = ion-exchanged catalyst, MEM = catalytic membrane.

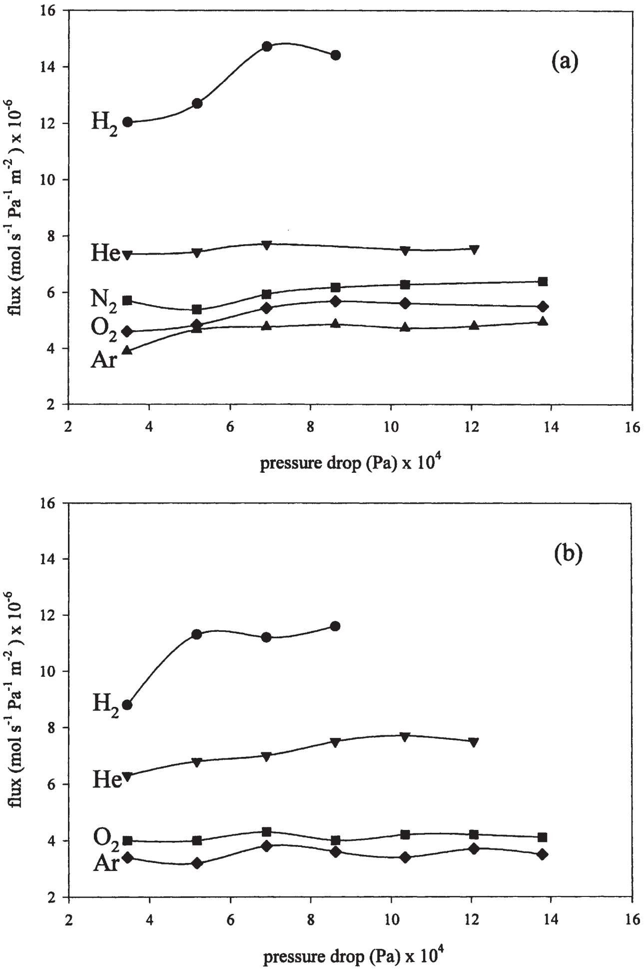

Figure 6. Results of flux experiment with pure gases for (a) SiO$_2$/γ-Al$_2$O$_3$ and (b) Pd/γ-Al$_2$O$_3$ membranes.

and it took eleven cycles to achieve a weight similar to the Pd/AlOOH membrane. This was due to the higher viscosity of the Pd/AlOOH solution. The total weight gain for each membrane was used to calculate the approximate thickness of the membrane, assuming that the density of the material was about 2.8 m^2/g. The Pd/γ-Al$_2$O$_3$ membrane was slightly thicker than the (PVA)/γ-Al$_2$O$_3$ membrane, as shown in the last column of table 1.

Other Pd/γ-Al$_2$O$_3$ samples were prepared including a sol–gel catalyst and an ion-exchanged catalyst. The physical properties of these samples are shown in table 2. The sol–gel sample and the membrane sample had almost identical characteristics including the Pd particle size, which was calculated from the chemisorption data to be about 3 nm. The ion-exchanged sample that was prepared using a commercial support had a surface area which was 50% lower, a larger pore diameter, and a higher dispersion of 41%. The particle size for this sample was calculated to be about 2.4 nm.

Table 3
Effect of temperature on the conversion of acetylene by a sol–gel Pd/γ-Al$_2$O$_3$ catalyst (10% C$_2$H$_2$/Ar at 20 ml/min, H$_2$ at 8 ml/min, 200 mg catalyst).

T (°C)	Conversion (%)	S_{ethylene} (%)
100	100	0
75	100	2
50	100	13
25	100	41

3.2. Flux measurements through SiO$_2$/γ-Al$_2$O$_3$ and Pd/γ-Al$_2$O$_3$ membranes

The results of flux experiments for the two membranes are shown in figure 6. The same scale for the y-axis is used for both plots. Overall the flux rates were slightly lower for the Pd/γ-Al$_2$O$_3$ membrane, and the trend in flux rates for both membranes was directly related to the molecular weight of the gases, suggesting a Knudsen diffusion mechanism. Since the size of the supported Pd particles was on the order of the size of the membrane pore, it was probable that the lower flow rates through the Pd/γ-Al$_2$O$_3$ membrane were due to pore plugging. Also the Pd/γ-Al$_2$O$_3$ membrane was more homogeneous and slightly thicker due to the higher viscosity of the Pd/AlOOH sol.

3.3. Activity of Pd/γ-Al$_2$O$_3$ catalysts in the hydrogenation of acetylene

The effect of temperature on the conversion of acetylene with the sol–gel Pd/γ-Al$_2$O$_3$ catalyst (SG) was investigated, and the results are shown in table 3. At 100 °C with excess hydrogen, acetylene was completely converted to ethane. As the temperature was decreased, the selectivity to ethylene increased but the total conversion remained 100%. The experiment was also performed with the ion-exchanged catalyst (IE). This catalyst exhibited complete conversion of acetylene to ethane at all of the tested temperatures (100–25 °C).

3.4. Hydrogenation of acetylene with the Pd/γ-Al$_2$O$_3$ membrane reactor

Shown in table 4 are the results of the hydrogenation of acetylene using the Pd/γ-Al$_2$O$_3$ membrane reactor at 100 °C. The flow rate of the 10% acetylene/Ar mixture was held constant at 20 ml/min inside the membrane tube. The flow rate of H_2 outside of the membrane (shell) was varied from 8 to 50 ml/min and was sometimes diluted with Ar. The amount of H_2 used was always in excess of the stoichiometric amount and was passed through the reactor in the same direction as the acetylene stream. The highest conversion of acetylene (79%) occurred when the ratio of H_2/C_2H_2 was 15, while the highest selectivity to ethylene occurred with an H_2/C_2H_2 ratio of 25. The last column of the table is an estimate of the amount of C_2 species that diffused to the shellside of the reactor. This value ranged from 39 to 58%.

Shown in table 5 are the results from hydrogenating acetylene with the membrane reactor in the premixed mode. In this case, H_2 was mixed with the acetylene stream and entered the reactor at the tube inlet. The gases passed through the membrane wall and exited at the shell outlet. The flow rates were kept constant ($H_2/C_2H_2 = 8$) and the temperature was varied from 100 to 200 °C. There was a balance between reaction temperature, conversion and selectivity. The highest conversion (91%) was found at 150 °C with a 71% selectivity to ethylene. The selectivity reached a maximum value of 85% at 200 °C. The increased selectivity achieved with the premixed feed can be explained by the decreased contact time between the acetylene and the catalyst, which was located in the membrane wall, as compared with a packed bed of catalyst. At 200 °C, the conversion decreased because the contact time had decreased to a point where the desorption of acetylene was faster.

Table 4
Conversion of acetylene and selectivity data for the Pd/γ-Al$_2$O$_3$ membrane reactor (10% acetylene/Ar tube at 20 ml/min, 100 °C).

F_{shell} (ml/min)	Fraction H_2 in shell flow (%)	H_2/C_2H_2	Conv. (%)	S_{ethylene} (%)	Loss of HC (%)
30	27	4	76	68	57
34	35	6	72	67	57
52	58	15	48	72	58
30	100	15	79	56	43
40	100	20	63	75	39
50	100	25	53	76	45

Table 5
Results from acetylene hydrogenation with Pd/γ-Al$_2$O$_3$ membrane reactor in premixed mode (10% C_2H_2/Ar at 10 ml/min, H_2 at 8 ml/min).

T (°C)	Conversion (%)	S_{ethylene} (%)
100	63	76
125	85	74
150	91	71
175	85	80
200	76	85

3.5. Activity of Pd/γ-Al$_2$O$_3$ catalysts in the hydrogenation of 1,3-butadiene

The two Pd/γ-Al$_2$O$_3$ catalysts were tested at 25 °C using a 10% 1,3-butadiene/Ar flow rate of 60 ml/min and a H_2 flow rate of 8 ml/min. The H_2/butadiene ratio was substoichiometric at a value of 1.3. If the ratio was increased to the stoichiometric value of 2 or more, the product of the reaction was almost 100% butane. The results of the experiment are shown in table 6. For the catalysts pretreated at 400 °C, a 96% conversion was achieved with a 32% selectivity to butenes. Because there may be a particle size effect with this reaction [19], the catalysts were exposed to flowing hydrogen at 650 °C for 22 h and then retested. Both catalysts became slightly more selective to the butenes while maintaining an almost 100% conversion of butadiene.

3.6. Hydrogenation of 1,3-butadiene with the Pd/γ-Al$_2$O$_3$ membrane reactor

For this experiment, the 10% 1,3-butadiene/Ar stream was passed through the membrane tube at a flow rate of 20 or 30 ml/min. H_2 was sometimes diluted in Ar and passed through the shellside of the reactor. The results are shown in table 7 for three different runs at 25 °C. The conversion of butadiene in all cases was nearly 100%. The highest selectivity to butenes occurred with a H_2 flow rate of 8 ml/min diluted with Ar at 22 ml/min on the shellside and a butadiene/Ar flow rate within the membrane tube of 20 ml/min. However, the loss of hydrocarbons through the membrane under these conditions was high (55%), so the Ar stream on the shellside was removed and the butadiene/Ar flow rate was increased to 30 ml/min. The data for this case is shown in the last line of table 7. The loss of hydrocarbons decreased to 40% while maintaining the high selectivity to the butene products.

The hydrogenation of 1,3-butadiene with the membrane reactor was also performed with the feed stream premixed with H_2 with the shell inlet and tube outlet closed. A constant H_2 flow rate of 8 ml/min was used and the flow rate of

Table 6
Conversion of 1,3-butadiene at 25 °C with traditional reactor (10% 1,3-butadiene/Ar at 60 ml/min, H_2 at 8 ml/min).

Sample	D_{H} (%)	Conversion (%)	S_{butenes} (%)
SG, O_2 H_2 400 °C	32	96	32
IE, O_2 H_2 400 °C	41	96	32
SG, H_2 650 °C	16	99	57
IE, H_2 650 °C	10	97	41

Table 7
Conversion of 1,3-butadiene at 35 °C with Pd/γ-Al_2O_3 membrane reactor.

F_{tube} (ml/min)	F_{shell} (ml/min)	Fraction H_2 in shell flow (%)	H_2/C_4H_6	Conv. (%)	S_{butenes} (%)	Loss of HC (%)
20	30	21	4	99	65	55
20	8	100	4	99	29	50
30	8	100	2.7	95	57	40

Table 8
Hydrogenation of 1,3-butadiene with the Pd/γ-Al_2O_3 membrane reactor in premixed mode ($T = 35\,^\circ$C, H_2 flow constant at 8 ml/min).

H_2/butadiene	Conversion (%)	S_{butenes} (%)
8	99	33
4	96	31
2	91	72
1.6	28	99

1,3-butadiene was changed in 10 ml/min increments. The results are shown in table 8. As the H_2/butadiene was decreased, the conversion of butadiene decreased but the selectivity to the butene products increased to almost 100%. This can again be explained by a shorter contact time between the reactants and the catalyst.

4. Summary and conclusions

Pd/γ-Al_2O_3 catalysts prepared by sol–gel processing are very active in the hydrogenation of acetylene and 1,3-butadiene. The Pd/AlOOH sol can also be used to successfully coat an α-Al_2O_3 substrate to form a mesoporous catalytic membrane capable of separating gases through Knudsen diffusion. The hydrogenation reactions performed by flowing a premixed feed through the Pd/γ-Al_2O_3 membrane wall resulted in the highest selectivity to the partially hydrogenated products while maintaining a high conversion without any loss of hydrocarbon species. For the acetylene reaction, an excess of H_2 was required ($H_2/C_2H_2 = 8$) at 200 °C to achieve a high selectivity to ethylene at a reasonably high conversion. In the hydrogenation of 1,3-butadiene, a high selectivity to the butene products occurred with a stoichiometric amount of H_2 ($H_2/C_4H_6 = 2$) at 35 °C. The increase in selectivity was attributed to a decrease in the contact time between the reactants and the catalyst.

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References

[1] J.N. Armor, Appl. Catal. 49 (1989) 1.
[2] M.P. Harold, C. Lee, A.J. Burggraaf, K. Keizer, V.T. Zaspalis and R.S.A. de Lange, MRS Bull. (April 1994) 34.
[3] V.M. Gryaznov and M.G. Slin'ko, Discuss. Faraday Soc. 72 (1982) 73.
[4] N. Itoh, W.-C. Xu and A.M. Sathe, Ind. Eng. Chem. Res. 32 (1993) 2614.
[5] C. Liu, Y. Xu, S. Liao and D. Yu, Appl. Catal. A 172 (1998) 23.
[6] C.J. Brinker, G.C. Frye, A.J. Hurd and C.S. Ashley, Thin Solid Films 201 (1991) 97.
[7] M. Chai, M. Machida, K. Eguchi and H. Arai, J. Membr. Sci. 97 (1994) 199.
[8] L.S. Benner, T. Suzuki, K. Meguro and S. Tanaka, *Precious Metals: Science and Technology* (The International Precious Metals Institute, Allentown, PA, 1991).
[9] G.C. Bond, *Heterogeneous Catalysis: Principles and Applications*, 2nd Ed. (Clarendon Press, Oxford, 1987).
[10] N.S. Schbib, M.A. Garcia, C.E. Gigola and A.F. Errazu, Ind. Eng. Chem. Res. 35 (1996) 1496.
[11] B.C. Gates, J.R. Katzer and G.C.A. Schuit, *Chemistry of Catalytic Processes* (McGraw-Hill, New York, 1979).
[12] W.K. Lam and L. Lloyd, Oil Gas J. 70 (1972) 66.
[13] C.E. Gigola, H.R. Aduriz and P. Bodnariuk, Appl. Catal. 27 (1986) 133.
[14] B.E. Yoldas, Ceram. Bull. 54 (1975) 289.
[15] C.K. Lambert and R.D. Gonzalez, Mater. Lett., in press.
[16] C.K. Lambert and R.D. Gonzalez, J. Mater. Sci., in press.
[17] J. Sarkany and R.D. Gonzalez, J. Catal. 76 (1982) 75.
[18] S. Ichikawa, H. Poppa and M. Boudart, J. Catal. 91 (1985) 1.
[19] B. Tardy, C. Noupa, C. Leclercq, J.C. Bertolini, A. Hoareau, M. Treilleux, J.P. Faure and G. Nihoul, J. Catal. 129 (1991) 1.