JOURNAL OF CATALYSIS **179,** 138–149 (1998)
ARTICLE NO. CA982224

The Effect of Ceramic Supports on Partial Oxidation of Hydrocarbons over Noble Metal Coated Monoliths[1]

A. S. Bodke, S. S. Bharadwaj, and L. D. Schmidt[2]

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

Received September 2, 1997; revised July 15, 1998; accepted July 17, 1998

Support effects on the production of synthesis gas and olefins by the partial oxidation of light hydrocarbons has been examined on noble metal catalysts at contact times of ~5 ms. We consider the effect of the following parameters on selectivities and conversions: adding a washcoat, varying pore size, ceramic support material, and loading of noble metal. In oxidation of methane on rhodium-coated monoliths, maximum hydrogen selectivity improves from 89 to 95% on the addition of a washcoat. It is also a strong function of the catalyst pore size, changing from 83% on a catalyst with 20 ppi (pores per inch) to 93% on a catalyst with 80 ppi. It varies from 86 to 91% on different ceramic supports with ZrO_2 giving the best results. Using *n*-butane as the fuel, the hydrogen selectivity improves from 70 to 95% on adding a washcoat and changes from 70 to 95% on changing the pore size. In the oxidation of ethane on platinum-coated monoliths, the addition of a washcoat reduces ethylene selectivity from 63 to 35%, while changing the pore size results in minor variations. On different ceramic supports, the ethylene selectivity varies from 60 to 64% with mullite giving the best results. We find that washcoat addition, decreasing pore size, and replacement of zirconia for alumina as the support material increase syngas selectivity and reduce olefin selectivity irrespective of the fuel, catalyst, or amount of diluent used. Most of these results can be explained on the basis of differences in mass transfer rates to the catalytic site between catalysts of different support geometries. It is argued that homogeneous reactions play a minor role in these short contact time processes.

INTRODUCTION

We have recently examined the partial oxidation of methane to syngas and ethane to ethylene over noble metal coated ceramic foam monoliths at contact times of the order of milliseconds and temperature of ~1000°C (1–3). In methane oxidation, the desired reaction is

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2, \quad \Delta H = -8.5 \text{ kcal/mol}.$$

We have shown that approximately 90% selectivity to syngas can be obtained at complete oxygen and >90% methane conversion over rhodium coated monoliths. In ethane oxidation, the desired reaction is the oxidative dehydrogenation to ethylene,

$$C_2H_6 + 1/2O_2 \rightarrow C_2H_4 + H_2O, \quad \Delta H = -25 \text{ kcal/mol}.$$

In this case, approximately 65% selectivity can be obtained at complete oxygen and 60% ethane conversion on platinum coated monoliths (4, 5). When Sn is added to Pt, selectivities as high as 70% can be obtained (6). These new processes offer several advantages over conventional processes for the production of syngas and olefins such as steam reforming and steam cracking (7, 8). They can be carried out autothermally, eliminating heat transfer problems. Also, they are very fast and require much smaller reactors.

We have typically used α-Al_2O_3 reticulated foam monoliths as catalyst supports. These consist of a single block of material with a continuous ceramic phase and a continuous pore phase. The pores have a fairly uniform size measured in pores per linear inch (ppi) and most experiments have been carried out on 45 ppi foams. Normal monoliths have very low surface areas (~1 m^2/g) compared to conventional catalysts, although washcoating can increase the surface area to ~10 m^2/g.

The effect of reactor configuration and catalyst geometry on the selectivities and conversions in partial oxidation reactions has been studied previously. Capannelli *et al.* compared the performance of packed bed, monolithic, and membrane reactors for the oxidative dehydrogenation of propane on V_2O_5/γ-Al_2O_3 catalyst (9). Hickman *et al.* compared alternate catalyst supports consisting of various materials, geometric configurations, and catalyst loading for HCN synthesis and NH_3 oxidation (10). Dietz *et al.* investigated syngas and olefin synthesis on ceramic foams, extruded ceramics, ceramic fibers, and woven gauze catalysts (11). In this study, we examine the effect of washcoat addition, changing pore size, support material, and catalyst loading on several important parameters in the above reactions.

EXPERIMENTAL

The reactor was essentially identical to that described previously and consists of a 1.8 cm diameter quartz tube (3).

[1] This research was supported by NSF under Grant CTS-962902.
[2] To whom correspondence should be addressed.

0021-9517/98 $25.00

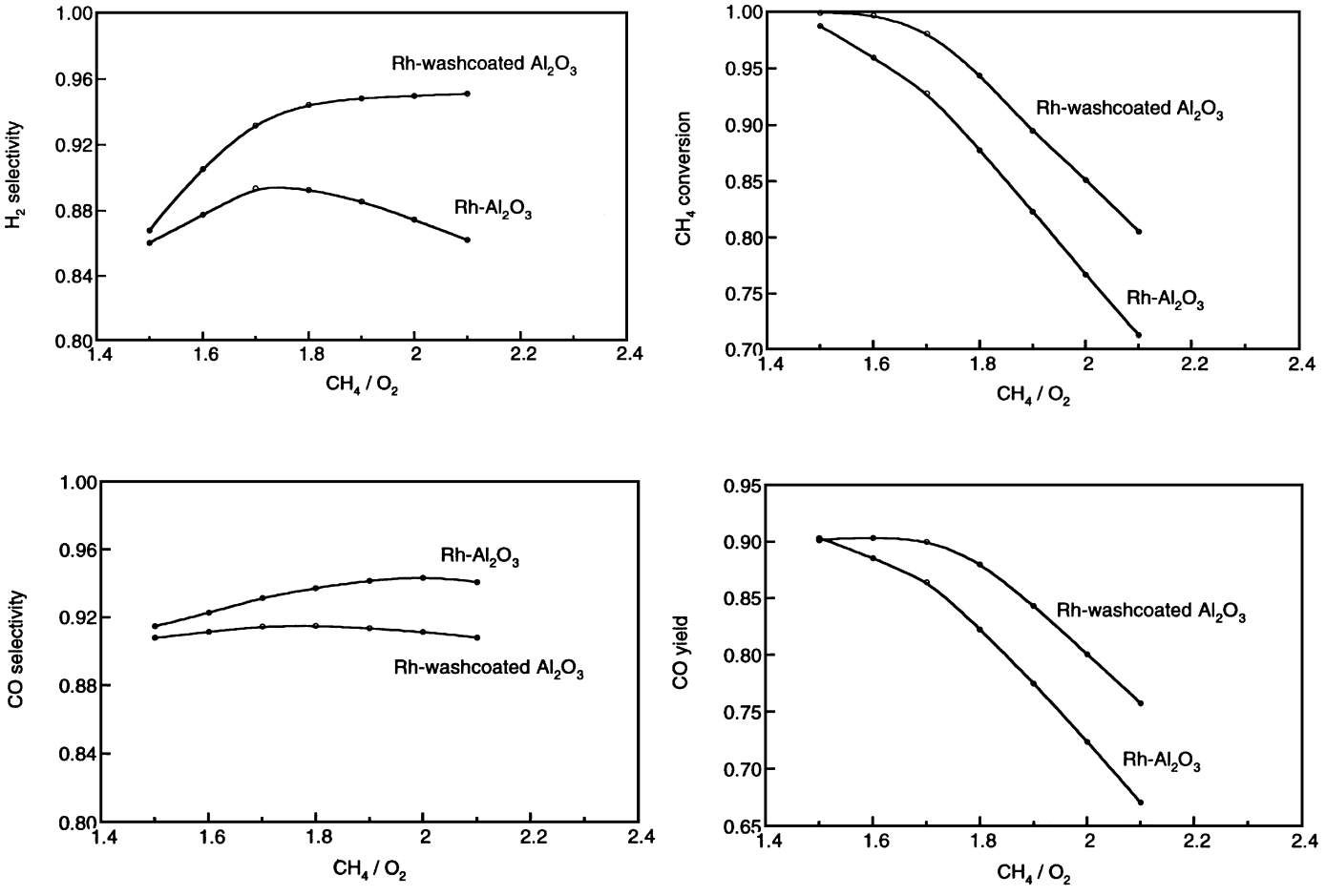

FIG. 1. Typical results for methane oxidation on Rh/Al_2O_3 and Rh/washcoated Al_2O_3 catalysts. H_2 and CO yields are higher on the washcoated catalyst.

The 1-cm long monolith catalyst was immediately preceded and followed by inert α-alumina monoliths of 45 ppi to minimize heat losses in the radial direction. Gases were fed at 20°C and no external heat was supplied. Bypass of the reactant gases around the catalyst was avoided by sealing the monoliths with a high temperature alumina-silica cloth. Temperatures were monitored by using a bare Pt/13% Rh thermocouple inserted from the rear end of the quartz tube between the catalyst and the back radiation shield. In experiments reported here, the total feed flow rate was always maintained at 5 slpm which corresponds to a residence time of ~5 ms. In all experiments, nitrogen dilution was 30% and the reactor outlet pressure was maintained at 1.2 atm, unless otherwise mentioned.

Product gases were fed through stainless steel lines to a sample loop of an automated gas chromatograph. The GC was a HP5890 with a 5A molecular sieve to separate O_2, N_2, CH_4, and CO and a Haysep D column to separate all other species. Nitrogen is an inert was added to the system as a GC calibration standard. The product gas C and H balances typically closed within ±5%.

Catalysts

Catalyst samples were prepared by impregnation of monoliths with a saturated solution of metal salt (H_2PtCl_6 in the case of Pt catalysts and $RhNO_3$ in the case of Rh catalysts). The samples were then dried overnight and calcined using a suitable procedure as described previously (4). Monoliths used in all experiments were obtained from Hi-Tech Ceramics Inc., Alfred NY. Alumina was used as the support for all pore size and washcoat experiments. Pore size has been varied from 20 ppi (average pore diameter of ~800 μm) to 80 ppi (~200 μm). The washcoat used in all experiments consisted of a thin layer of γ-alumina (~30–50 μm) applied subsequent to the preparation of the monolith. To study the effect of support material, foam monoliths prepared from various ceramic materials were obtained. These include α-alumina (92% Al_2O_3, 8% SiO_2), mullite (63% Al_2O_3, 37% SiO_2), zirconia, zirconia-tetra-alumina or ZTA (20% ZrO_2, 80% Al_2O_3), oxide-bonded silicon carbide, or OBSiC (50% SiC, 40% Al_2O_3, 10% SiO_2), cordierite (15% MgO, 35% Al_2O_3, 50% SiO_2) and

lithium aluminum silicate or LAS (4% LiO_2, 29% Al_2O_3, 67% SiO_2). All these supports were nominally identical in terms of pore size (45 ppi), void fraction (~80%) and dimensions (18-mm diameter and 10-mm length). Scanning electron micrographs of these supports indicated comparable geometries, although different materials had different roughness on a microscale as will be discussed later.

RESULTS

Methane Oxidation

Typical results for methane oxidation on a Rh/Al_2O_3 catalyst can be seen in Fig. 1. On changing fuel/oxygen ratio from 1.5 to 2.1, CO selectivity rises from 91 to 94% while H_2 selectivity stays at ~86%. Methane conversion drops from 99 to 70%. The effect of Rh loading on methane oxidation has been reported previously (17). It was found that selectivities and activities remain identical for Rh loadings between 1 and 15%. In all experiments described here, Rh loading is maintained considerably higher than 1%.

Figure 1 also compares results on a washcoated Rh catalyst to the one mentioned above. Compared to the normal catalyst, we see an improvement in maximum H_2 selectivity from 89 to 95% accompanied by a decrease in CO selectivity from 94 to 92%. Methane conversion is higher and temperature is lower on the washcoated catalyst. This result has been reproduced on three different samples of washcoated catalysts. Although the selectivity to CO decreases on adding a washcoat, the yield is higher because of greater fuel conversion.

Results of catalysts with different pore sizes are compared in Fig. 2. H_2 selectivity and CH_4 conversion are seen to increase as the pore size is reduced. Although no trend in CO selectivity can be observed, the yield is higher on catalysts with smaller pore size. Thus, decreasing the pore size also results in greater syngas yield.

Figure 3 compares Rh catalysts prepared on different supports. Cordierite and lithium aluminum silicate ceramics have low melting points and can withstand temperatures up to 1000°C only. Catalysts made on these supports melt as soon as ammonia introduced for startup is removed. It is seen that zirconia-supported catalysts give better H_2 selectivity than those supported on alumina. Again, CO yields follow the same sequence as do H_2 selectivities (and yields).

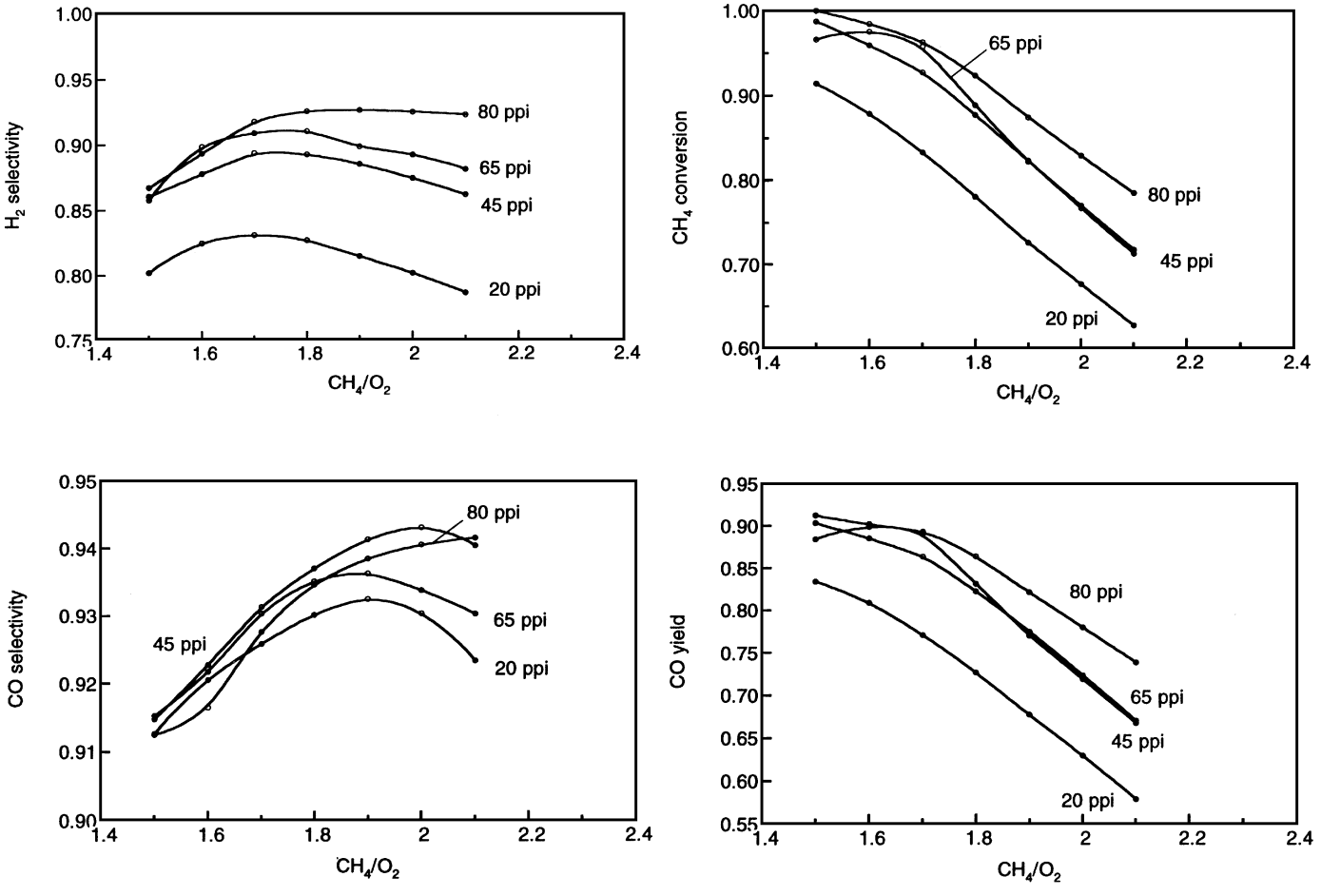

FIG. 2. Effect of pore size of Rh/Al_2O_3 catalyst on methane oxidation. Smaller pore size gives better syngas yields.

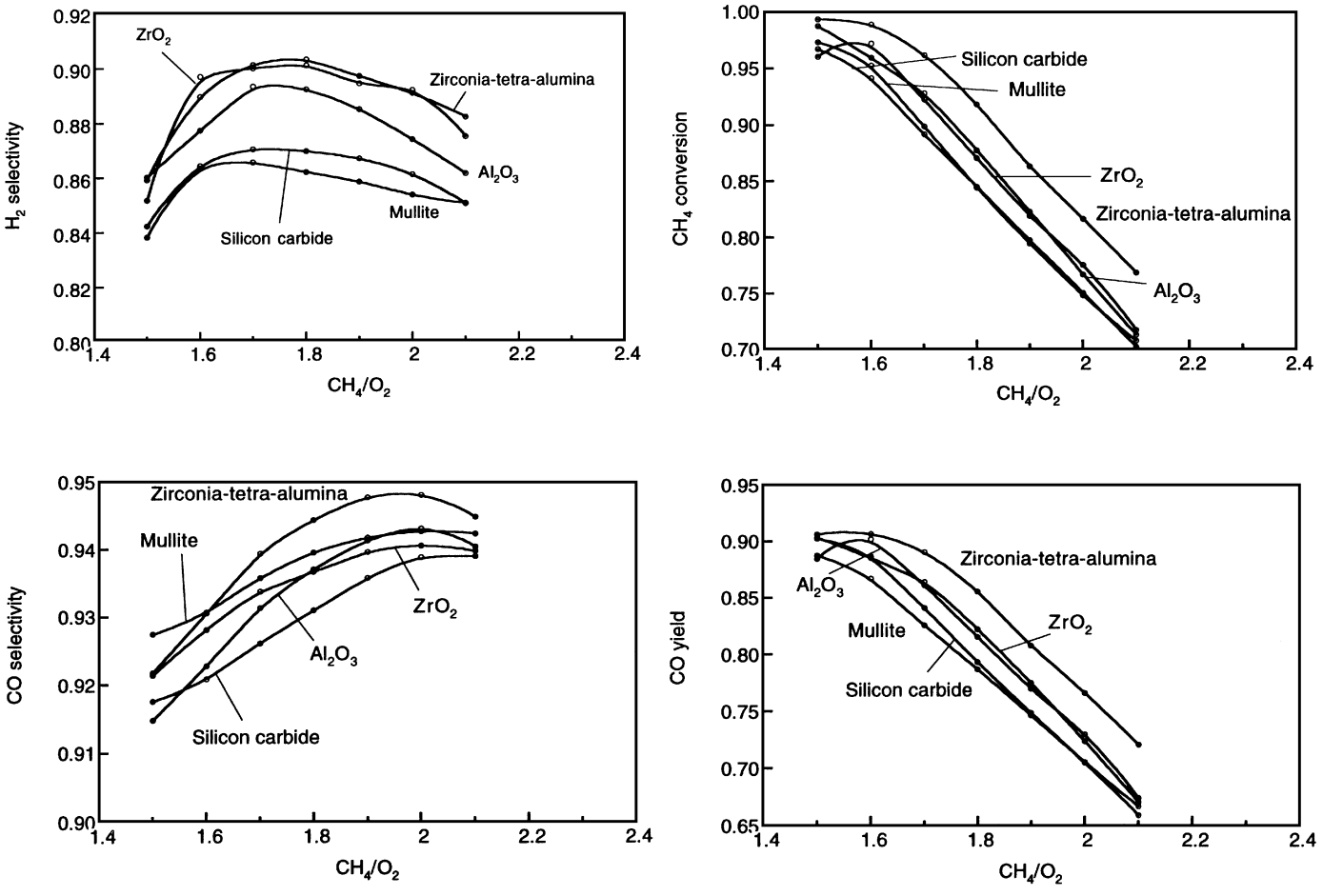

FIG. 3. Effect of support material on methane oxidation. Rh catalysts prepared on zirconia containing supports give higher syngas yields than alumina containing supports.

ZrO_2 can withstand temperatures of up to 2000°C and this is an added advantage in using ZrO_2 containing monoliths to prepare the catalyst.

Ethane Oxidation

Typical results for ethane oxidation on Pt/Al_2O_3 can be seen in Fig. 4. Ethylene selectivity rises from 57 to 63% while ethane conversion drops from 92 to 62% on increasing the fuel/oxygen ratio. We have carefully studied the effect of loading on this process. To eliminate other effects, five monoliths with identical weights were selected out of 30 samples and were loaded at the same time to give catalysts of approximately 5, 3, and 1% loading of platinum (actual loadings were 5.1, 5.3, 5.5, 2.7, and 0.96%). Care was taken to carry out the experiments in an identical manner. Figure 4 compares important parameters on these five catalysts.

It is seen that 1% Pt catalyst gives better C_2H_4 selectivity (64.6%), as compared to 3% Pt catalyst (63.7%) and 5% Pt catalyst (63.5%). Conversion also follows a similar trend as C_2H_4 selectivity. These results show that lower loadings give better C_2H_4 selectivity and ethane conversion but that the improvement is very small. In all experiments described below, we have maintained Pt loading above 1% to eliminate possible loading effects.

Figure 5 shows C_2H_4 and CO selectivity, ethane conversion, and temperature on a washcoated Pt catalyst superimposed on the results of a typical Pt/Al_2O_3 catalyst. We see a large deterioration in C_2H_4 selectivity and ethane conversion accompanied by a consequent increase in CO selectivity on the washcoated catalyst. Results of Pt catalysts with different pore sizes are presented in Fig. 6. C_2H_4 and CO selectivity increase with decrease in pore size with 80-ppi catalyst giving maximum selectivity, although the difference is very small.

Figure 7 compares Pt catalysts prepared on different support materials. We see better C_2H_4 selectivity on mullite followed by α-Al_2O_3 supports. Zirconia-containing supports give lower C_2H_4 selectivity than alumina-based materials. Conversions also follow the same trend but the trend is reversed for CO selectivity with the catalyst on zirconia support giving the highest CO selectivity. Recalling results

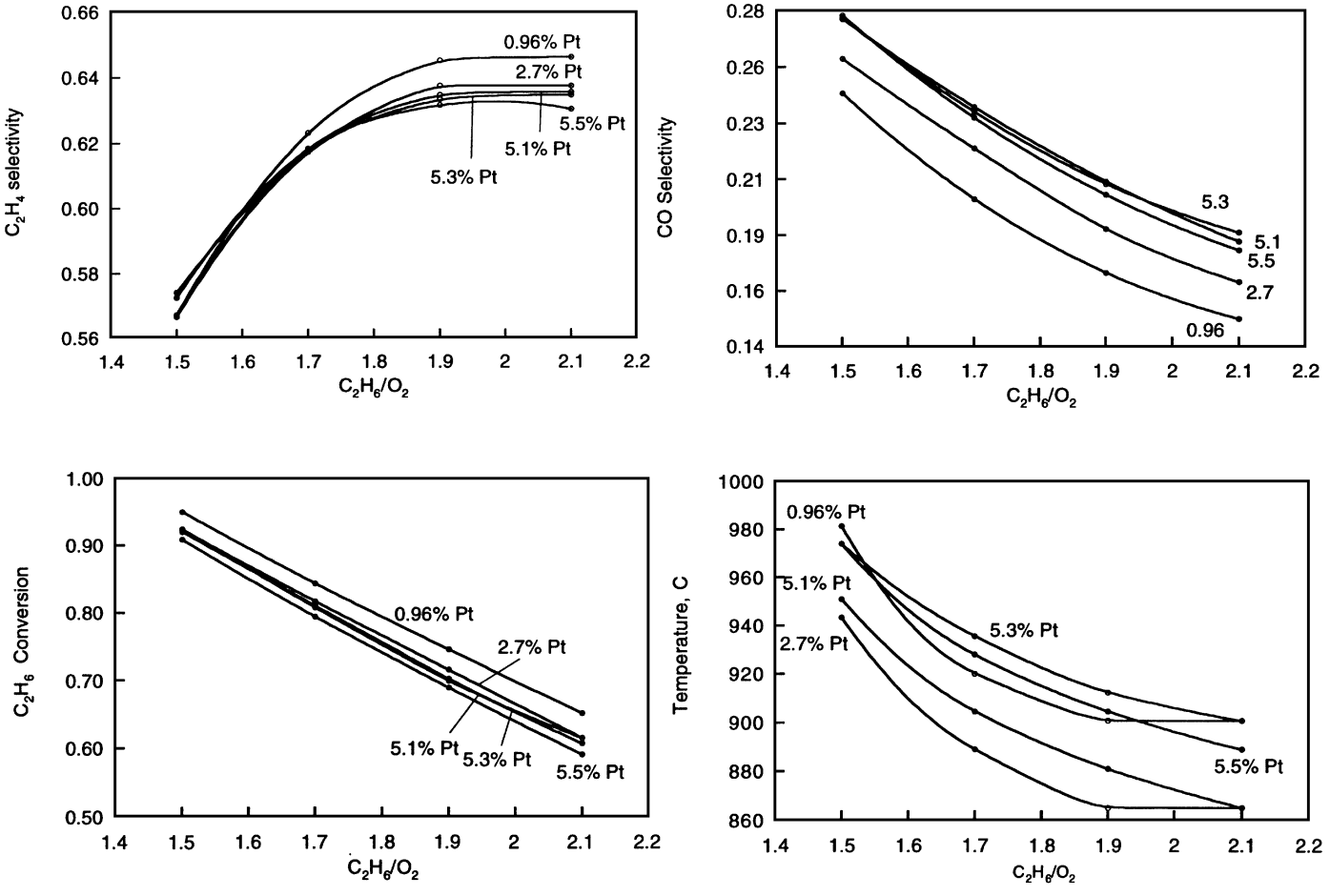

FIG. 4. Typical results for ethane oxidation on Pt/Al_2O_3 catalysts with different loadings.

in the methane oxidation process, we see that support selection here is reversed in order, since ethylene is the desired product.

n-Butane Oxidation

Typical results for *n*-butane oxidation in air on Rh/Al_2O_3 can be seen in Fig. 8. CO and H_2 selectivity decrease from 80 to 40% and 70 to 20% on increasing butane/oxygen ratio, while ethylene selectivity rises from 5 to 25%. Figure 8 also compares results on a washcoated Rh catalyst with the Rh/Al_2O_3 catalyst. We see a large rise in H_2 and CO selectivity and a drop in C_4H_{10} conversion upon adding a washcoat to the Al_2O_3 monolith. Operation at butane/oxygen $=0.45$ is particularly attractive with 98% conversion, 95% H_2 selectivity, and no production of higher hydrocarbons.

Figure 9 compares catalysts of different pore sizes prepared under otherwise identical conditions. The figure shows that the H_2 and CO selectivity increase and the fuel conversion decreases with decreasing the pore size. Lower conversion on monoliths with smaller pores is a result of lower C_2H_4 and higher CO selectivity, requiring a greater amount of oxygen and, thus, reducing the fuel consumption.

We see that the effect of adding a washcoat and decreasing the pore size in *n*-butane oxidation on Rh catalysts follows the same trends as they did in methane oxidation described at the start of this section. Also note that oxygen conversion is always complete in all these processes.

DISCUSSION

The above results indicate that washcoat addition, decreasing pore size, and replacing alumina by zirconia in the support material increase the syngas production and simultaneously reduce the olefin yield, irrespective of the fuel, catalyst, or amount of diluent, although the effect of washcoat and pore size is much greater than the support material. Also, noble metal loading has a very small effect on the selectivities and conversions in these reactions.

Monolithic partial oxidation processes are considerably different from those in conventional packed bed processes (12). These reactions are exceedingly fast and go to essentially complete conversion of the limiting reactant even at millisecond contact times. Conversions are independent of the flow rates over more than a factor of 10 in the flow

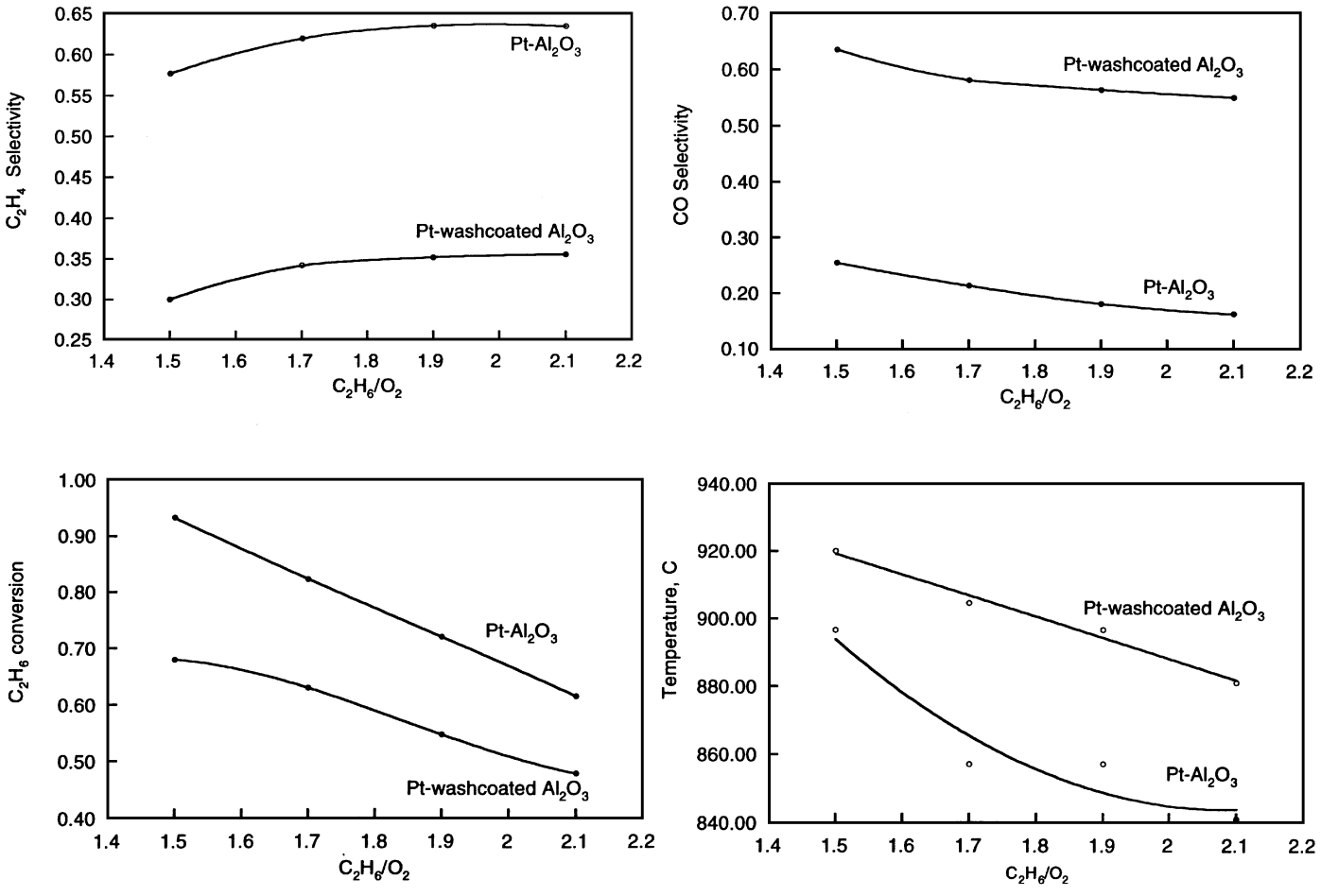

FIG. 5. Effect of adding a washcoat to Pt/Al_2O_3 monolith on C_2H_6 oxidation. Adding a washcoat considerably reduces C_2H_4 selectivity and C_2H_6 conversion and produces more CO.

rate, which suggests that catalyst surface area is unimportant in determining the yield of the desired product (13). At 1000°C, assuming a kinematic viscosity of ~2 cm^2/s, superficial velocity of ~10 m/s, and average pore size of ~0.05 cm, the Reynolds number of gas flow is 25. Hence, gas flow in the monolith structure should be laminar under these experimental conditions in all catalysts. Since surface reaction rates are very fast, the process is limited either by rate of adsorption or mass transfer of the limiting reactant to the catalyst surface.

Hickman and Schmidt propose a purely heterogeneous mechanism to explain the results of methane oxidation on Rh monoliths (14). They used a multistep model with a sequence of adsorption, surface reaction, and desorption steps, with reaction parameters obtained from the literature or fitted to previous experiments. According to this model, CH_4 and O_2 molecules adsorb dissociatively on the catalyst to give C_s, H_s, and O_s surface species. C_s adatoms react with O_s adatoms to produce CO and CO_2 in successive steps. Similarly H_s adatoms react with O_s to form OH_s and then H_2O or react with H_s to form H_2. The simulated results from this 18-step model were in pretty good agreement with experimental results on Pt and Rh catalysts. Syngas is an equilibrium product at high temperatures. In partial oxidation process, it is an intermediate and oxygen should be very quickly consumed before it can react with CO and H_2 to form CO_2 and H_2O.

This model was extended by Huff and Schmidt to the oxidative dehydrogenation of ethane on Pt monoliths (15). Here, C_2H_6 was assumed to adsorb dissociatively to form C_2H_{5s}, H_s, and OH_s surface species. β-elimination of the H-atom of adsorbed C_2H_{5s} results in C_2H_4 formation. C_2H_4 can further decompose to form graphite on the solid surface or react with oxygen to produce CO or CO_2. Only a few percentages of ethylene is predicted at thermodynamic equilibrium. Graphite is a stable solid product and the gas phase mixture should predominantly contain syngas at equilibrium. Ethylene should therefore be removed from the catalyst as soon as it is formed to prevent it from reacting further to give unwanted products.

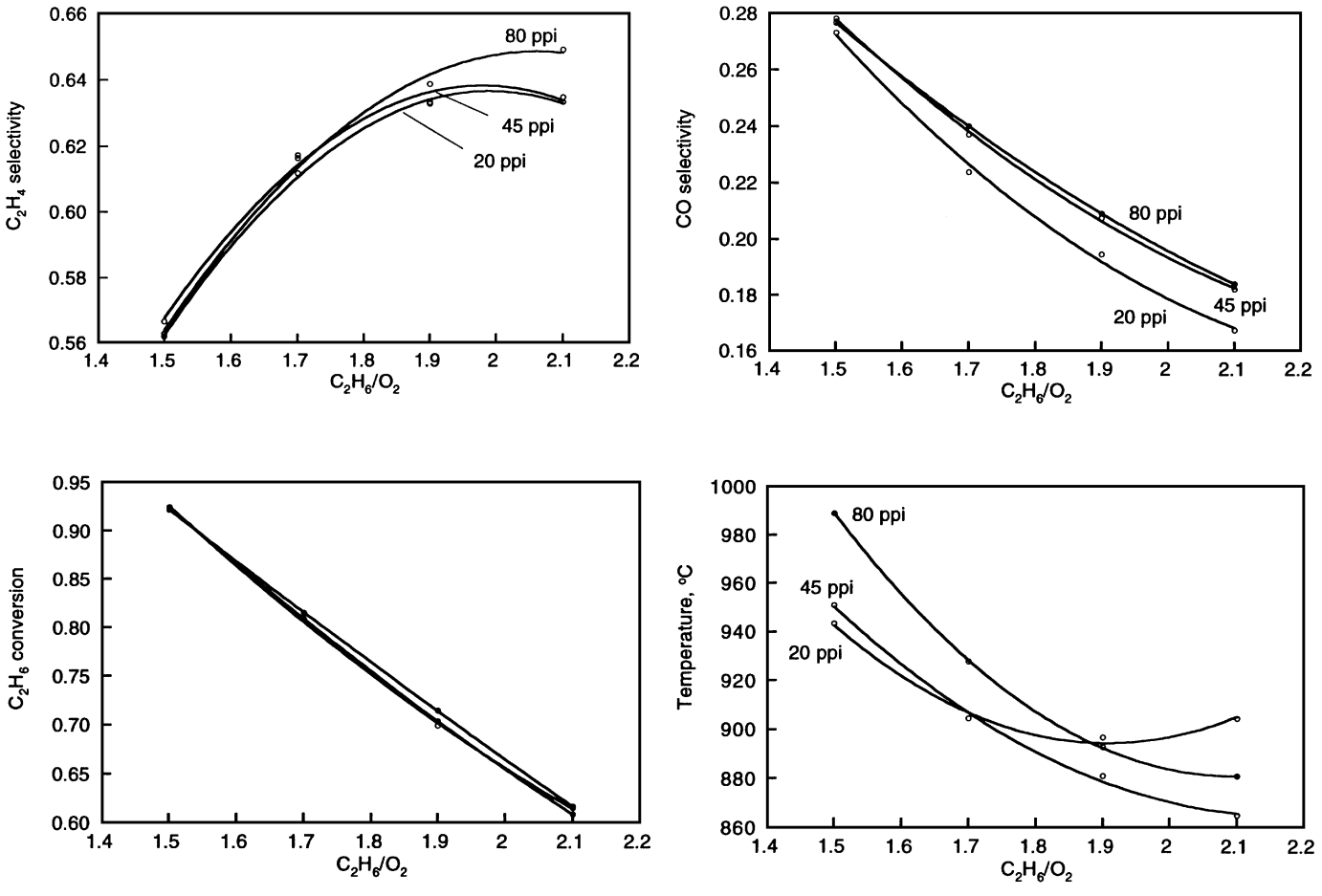

FIG. 6. Effect of pore size of Pt monoliths on ethane oxidation. Smaller pores give slightly higher ethylene selectivity and ethane conversion.

Pore Size

Under laminar flow conditions, the Sherwood number will be independent of Reynolds number as a first approximation (16). If we approximate the monolith structure as a number of cylindrical tubes of equivalent diameter, d, then one would expect

$$k_m = D/\delta$$
$$= 2D/d,$$

where k_m is the mass transfer coefficient, D is the diffusion coefficient, and δ is the boundary layer thickness. Consequently, the rate of mass transfer of reactants to the catalyst surface will be higher for catalysts with smaller pore size than those with larger pores. Since oxygen conversion is always complete, in methane and *n*-butane oxidation this will mean that oxygen is quickly reacted in the early part of the catalyst before it can react with CO and H_2 to form CO_2 and H_2O. The more rapid predicted conversion of O_2 appears to explain the higher syngas yields on catalysts with smaller pores.

In ethane oxidation on Pt catalysts, better mass transfer of oxygen to the surface will enhance the formation of C_2H_4 and CO and consume more oxygen in the process, leaving less oxygen for the oxidation of these molecules to form CO_2. Hence, we observe an increase in C_2H_4 and CO yields and a consequent decrease in CO_2 yield on reducing the pore size, although this effect is much smaller than that in CH_4 oxidation.

Washcoat

Application of a washcoat to the monolith roughens the surface and adds microporosity to the walls of the catalyst. This is expected to increase mixing in the reactant gases which will improve mass transfer of the limiting reactant (oxygen) to the catalyst surface. Thus, we should obtain improved syngas yields in methane and butane oxidation. Experiments were carried out on washcoated catalysts prepared on 45-ppi foams, where the average pore size is 450 μm. The washcoat thickness is approximately 30–50 μm while the surface irregularities are expected to be of the order of 2–3 μm. Although the effect of surface roughening on mass transfer is not expected to be very large for laminar flows (12), the increase in surface area of Rh due to washcoating could also be responsible for improved

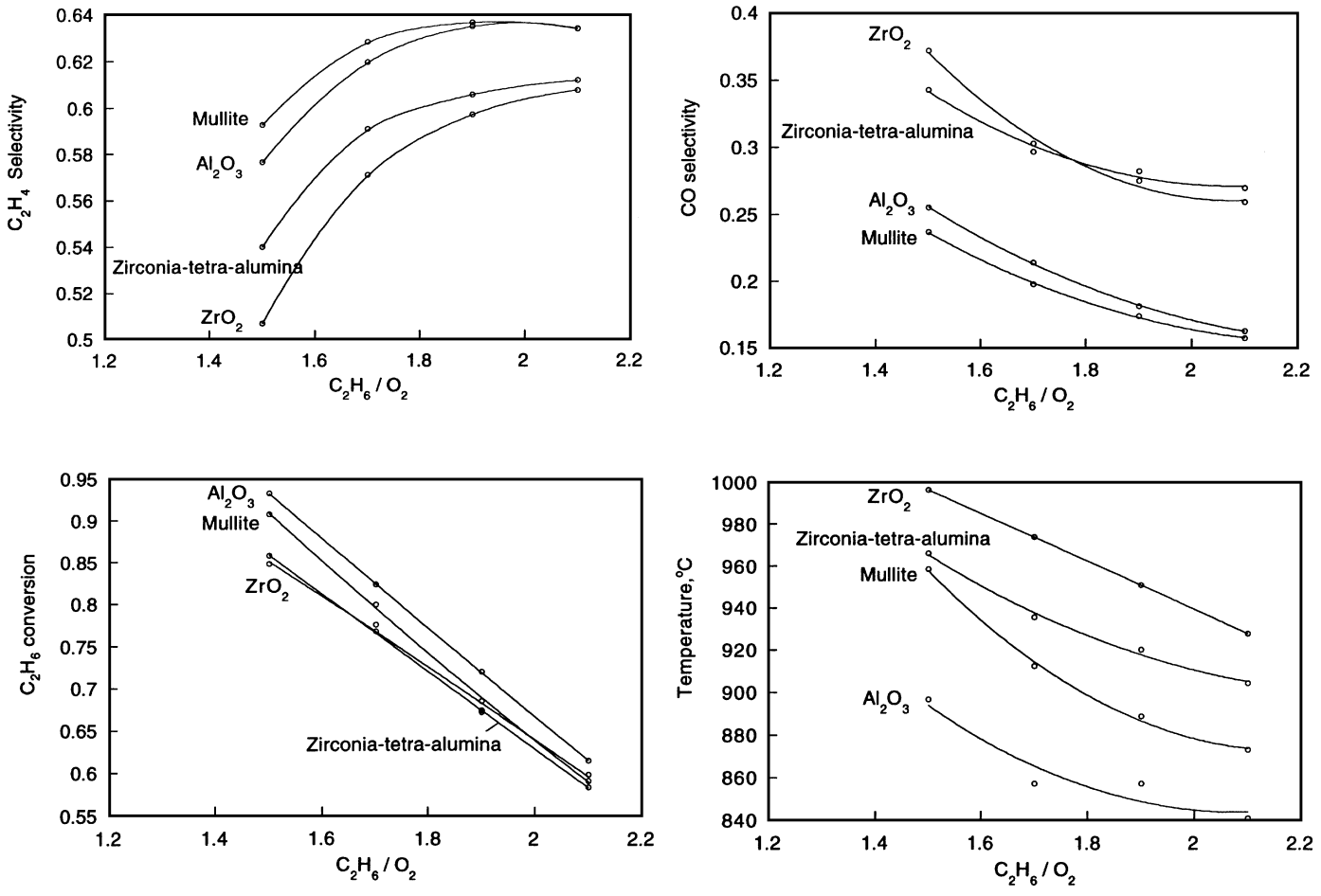

FIG. 7. Effect of support material on ethane oxidation. Alumina-containing supports give higher ethylene selectivity and ethane conversion than zirconia-containing supports.

syngas yields since Rh is known to promote CO and H_2 production.

In ethane oxidation, ethylene should be removed from the reactor as soon as it is formed to maximize its yield. On washcoated catalysts, ethylene could get trapped in the microporosity on the washcoated surface. This could lead to decomposition to form graphite or further reaction with oxygen to form CO and CO_2 which explains the considerable reduction in ethylene selectivity on washcoated catalysts.

Alternately, γ-Al_2O_3 on the monolith surface could itself be catalytically active and could favor the formation of syngas, whose yield is found to increase on the washcoated surface irrespective of the noble metal used as catalyst. We believe this effect to be small because the γ-Al_2O_3 should be rapidly converted to α-Al_2O_3 at reaction temperatures.

Catalyst Loading

We find that changing Pt or Rh loading between 1 and 10% has a small effect on selectivity and conversion (17). In fact, coating only the front face of the foam with noble metal also gives comparable results to a uniformly coated catalyst. This leads us to believe that partial oxidation reactions on noble metals proceed extremely rapidly, and a minimum loading of these metals is sufficient to achieve nearly the optimum selectivity and conversion.

Support Material

The support is usually an inert surface that provides a means of spreading out the metal catalyst for its most effective use. In some cases, the support may actually contribute catalytic activity, depending on the reaction and reaction conditions. In the reactions considered here, however, the effect of changing support material was observed to be small, probably smaller than the effect of catalyst geometry. Changing the noble metal catalyst, on the other hand, has a large effect on the results. Pt catalysts give significant olefinic products, Rh catalysts give maximum selectivity to syngas, while Pd catalysts coke rapidly.

Panels (a) and (b) of Fig. 10 show SEM micrograph images of ~1% Pt/ZrO_2 and ~5% Rh/Al_2O_3 catalyst after several hours of operation. Panels (c) and (d) show surfaces

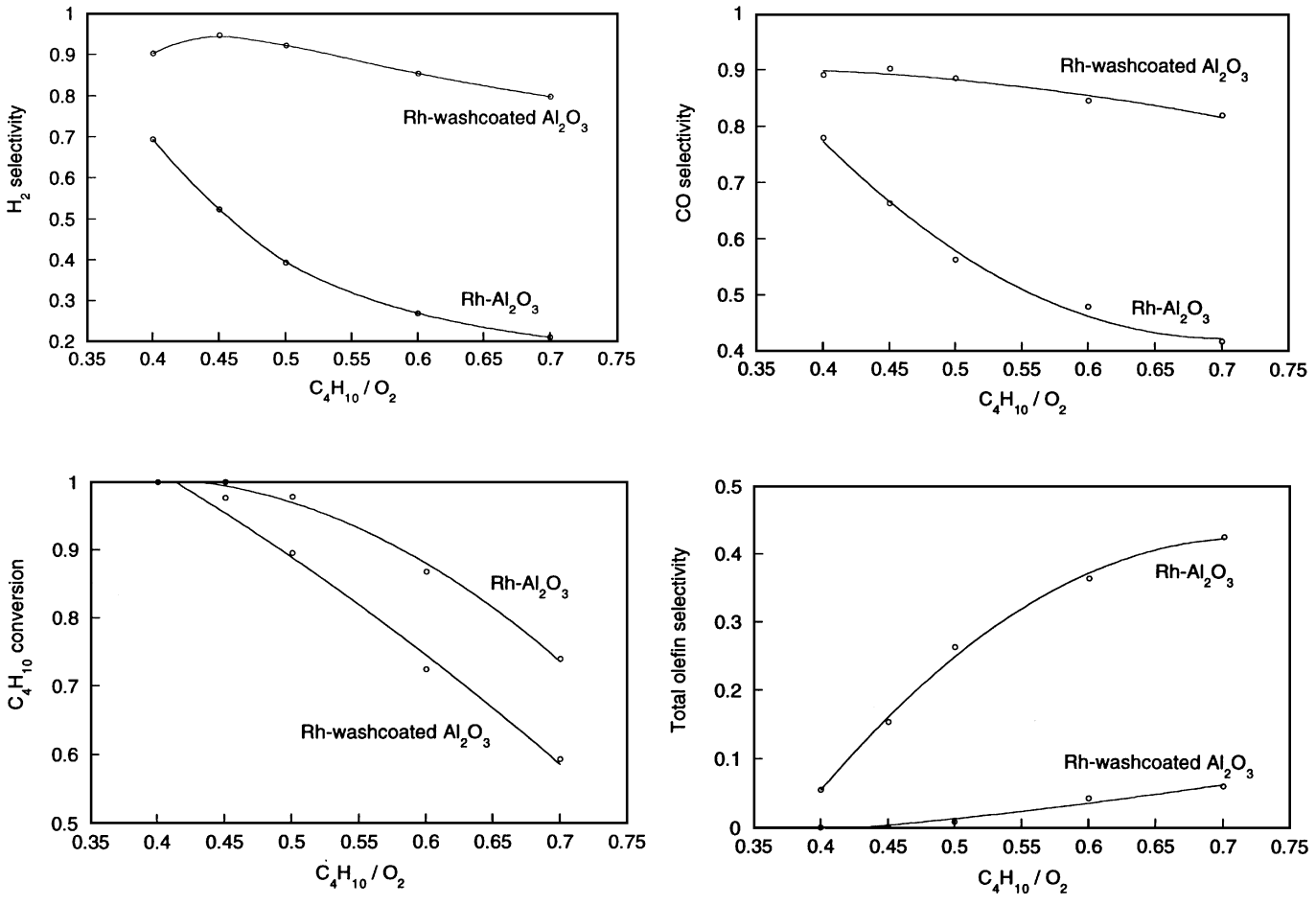

FIG. 8. Typical results for *n*-butane oxidation on Rh/Al_2O_3 and Rh/washcoated Al_2O_3 catalysts. H_2 and CO selectivity are higher on washcoated catalyst.

of ZrO_2 and Al_2O_3 supports without metal loading. These images show that the noble metal exists as small crystalline particles on the surface. The size of the crystalline particles was observed to be about 1 μm for both Pt and Rh and was nearly independent of the loading or support. It can also be seen that the morphology of the ZrO_2 and Al_2O_3 supports is considerably different with alumina exhibiting finer grain size ($\sim$2 μm) than ZrO_2 ($\sim$6 μm). The surface of ZrO_2 foams appears rougher than Al_2O_3 on that size scale. The differences observed on various support could be largely a consequence of the different surface characteristics rather than differences in any catalytic properties of the ceramic materials. ZrO_2 foams and washcoated alumina have microscopically rougher surface, and thus give greater selectivity to syngas, compared to catalysts prepared on Al_2O_3 foams.

The Role of Homogeneous Chemistry

The contribution from homogeneous chemistry in catalytic partial oxidation reactions has been a subject of much attention (2, 5, 23, 24). We have previously argued that heterogeneous reactions dominate in these short contact time processes. This has been based on observations that catalysts prepared with different noble metals behave very differently (25), feed mixtures in these experiments are far outside flammability limits, ignition delay time of gas phase reactions are of the order of 10 ms, and the walls of the monolith catalyst should provide a high surface area to scavenge free radical homogeneous reaction propagators. Although experiments carried out here indicate that these high-temperature oxidation reactions appear to be controlled by the transport of reactant species to the catalyst surface, they do not give much insight to the contribution of homogeneous chemistry; 20 ppi catalysts have much greater void fraction than 80 ppi catalysts and there should be less diffusion of radicals and heat to the walls. Therefore more gas-phase chemistry is expected to occur inside the larger channels of these monoliths. However, very slight difference in behavior of Pt catalysts prepared on 20 and 80 ppi monoliths are experimentally observed which is consistent with our previous argument that these reactions are predominantly heterogeneous.

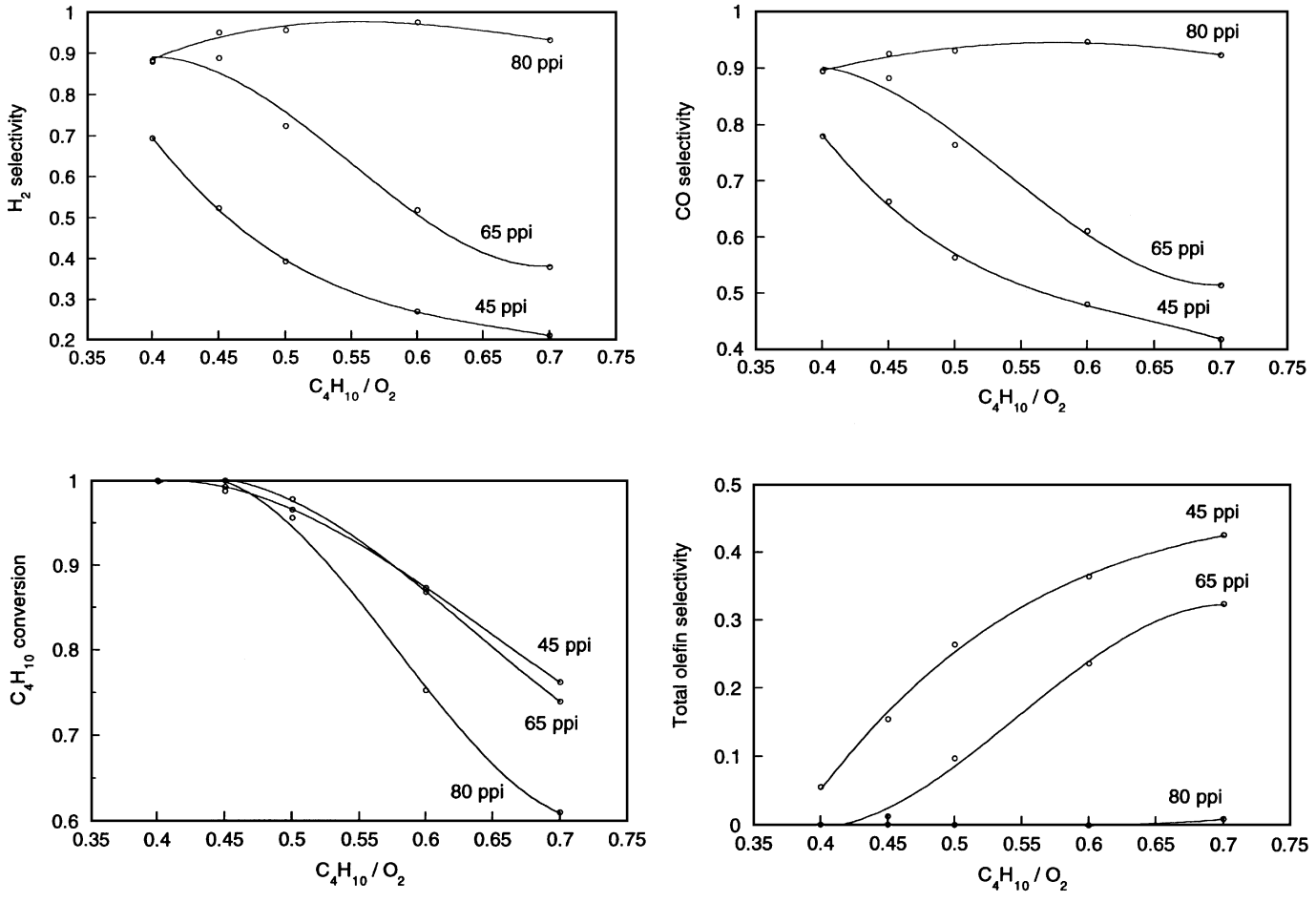

FIG. 9. Effect of pore size on *n*-butane oxidation. H_2 and CO selectivity rise, conversion drops on monoliths with smaller pores.

In contrast to these experiments, recent results show that there is a considerable oxygen breakthrough in the oxidation of higher alkanes such as pentane and hexane (26). Quenching of reaction gases after the catalyst decreases oxygen and fuel conversion. In oxidation of C_1-C_4 hydrocarbons on woven noble metal gauze, the contact time is of the order of $\sim 10^{-5}$ ms (27). The high transparency (81%) of the gauze, combined with short contact times, leads to a

TABLE 1

Physical Properties of Some Ceramic Support Materials

Support material	Melting point (°C)	Thermal conductivity	Thermal shock resistance[a] (gm)	Compressive strength (psi)	Modulus of rupture[b] (psi)	Thermal expansion (10^{-6}/°C)
Mullite	1700	high	1.1	108	160	—
α-Al_2O_3	1870	high	1.3	301	418	7.5
Zirconia tetra alumina	2100	low	0.9	181	150	8.0
Stabilized ZrO_2	2470	low	0.4	146	256	7.9
Silicon carbide	1720	v. high	0.1	155	240	5.5
Cordierite	1470	—	0.0	215	192	2.0
Lithium aluminum silicate	1367	—	0.0	150	190	1.2

[a] Weight loss after sample was rapidly heated to 1800°F and cooled to room temperature.
[b] Determined by 3-point bend test.

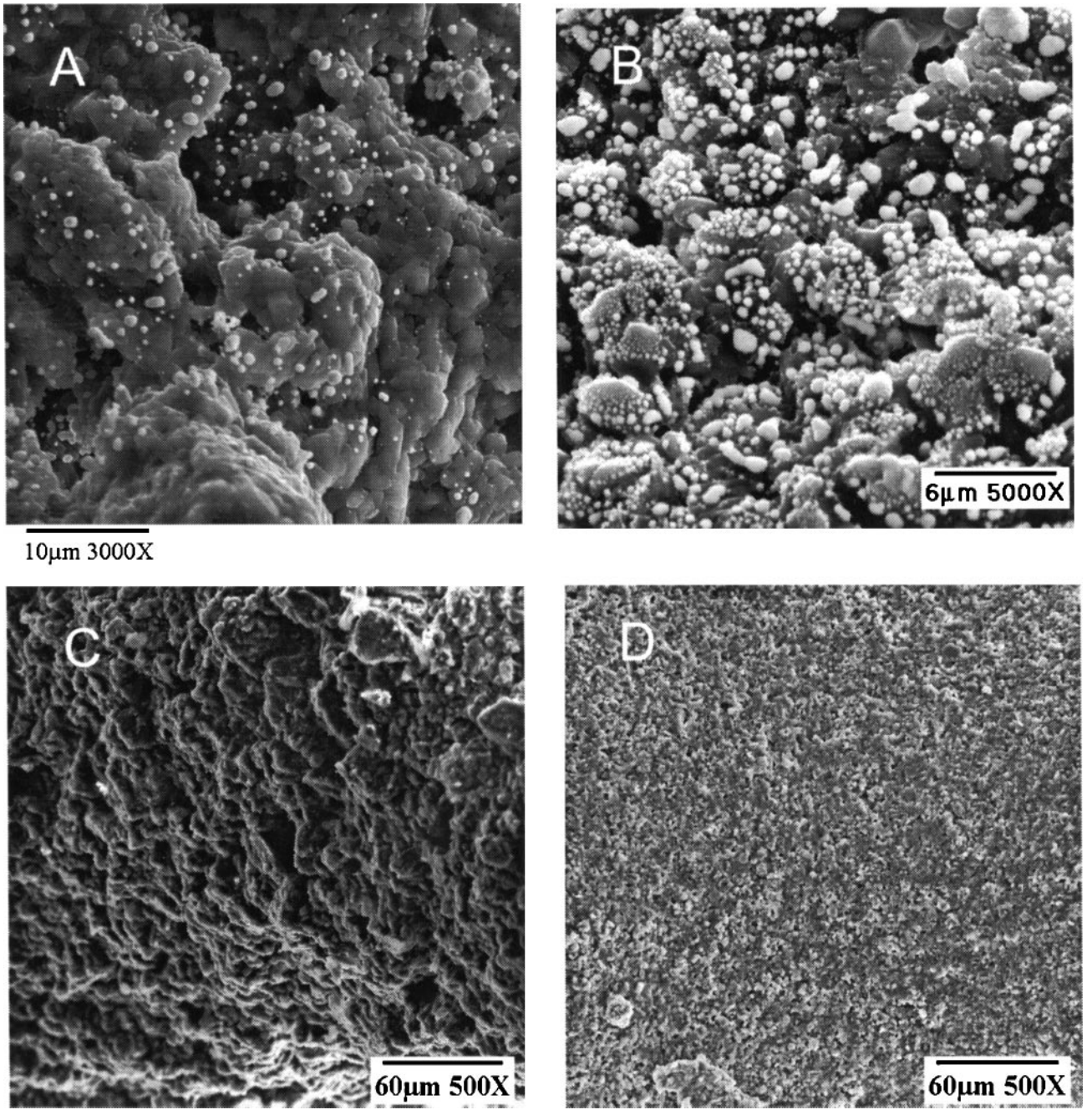

FIG. 10. SEM micrograph images: (a) 1% Pt/ZrO_2, (b) 5% Rh/Al_2O_3, (c) ZrO_2, (d) Al_2O_3. The noble metal exists as crystalline, aggregated particles on the ceramic surface. The surface of ZrO_2 is rougher than that of Al_2O_3 foam.

significant amount of reactants passing between the catalytic wires. High oxygen conversion is achieved with a single layer of gauze despite this fact. Significant homogeneous chemistry could be occurring in both these processes.

CONCLUSION

The choice of catalyst metal is undoubtedly the most crucial factor determining yield of the desired product in all these processes. These experiments indicate that support geometry may also affect the performance considerably. The addition of a washcoat tends to increase CO and H_2 yields for any fuel, catalyst, or diluent. If syngas is desired, adding a washcoat is preferred; if intermediates such as olefins are desired, then use of a nonwashcoated catalyst is preferred. Decreasing pore size increases CO and H_2 yields on Rh catalysts and also increases ethylene yields on Pt catalysts. The smallest possible pore size should be used in either

case, which will be limited by pressure drop constraints or by limitations in the manufacturing process. Changing support material does not strongly affect the production of desired products in these processes. It would be more appropriate to choose the right kind of support, depending on the operating conditions such as reaction temperature, thermal expansion requirements, etc. An argument based on change in mass transfer rates on catalysts with different support geometries explains most of the experimental results. We also suggest that homogeneous chemistry plays a minor role in these reactions, at least for small alkanes.

REFERENCES

1. Hickman, D. A., and Schmidt, L. D., *Science* **259**, 343 (1993).
2. Hickman, D. A., Haupfear, E. A., and Schmidt, L. D., *Catal. Lett.* **17**, 223 (1993).
3. Hickman, D. A., and Schmidt, L. D., *J. Catal.* **138**, 267 (1992).
4. Huff, M., and Schmidt, L. D., *J. Phys. Chem*. **97**, 11815 (1993).
5. Huff, M., and Schmidt, L. D., *Catal. Today* **21**, 443 (1994).
6. Yokoyama, C., Bharadwaj, S., and S., Schmidt, L. D., *Catal. Lett.* **38**, 181 (1996).
7. Weissermel, K., and Arpe, H. J., "Industrial Organic Chemistry," VCH, Weinheim/New York, 1993.
8. Twigg, M. V., "Catalyst Handbook," Wolfe, London, 1989.
9. Capannelli, G., Carosini, E., Cavani, F., Monticelli, O., and Trifiro, F., *Chem. Eng. Sci.* **51**, 1817 (1996).
10. Hickman, D. A., Huff, M., and Schmidt, L. D., *Ind. Eng. Chem. Res.* **32**, 809 (1993).
11. Dietz, A., and Schmidt, L. D., *Mat. Res. Soc. Symp. Proc.* **368**, 299 (1995).
12. Cybulski, A., and Moulijn, J. A., *Catal. Rev.-Sci. Eng.* **36**, 179 (1994).
13. Witt, P. M., and Schmidt, L. D., *J. Catal.* **163**, 465 (1996).
14. Hickman, D. A., and Schmidt, L. D., *AIChE J.* **39**, 1164 (1993).
15. Huff, M. C., and Schmidt, L. D., *AIChE J.* **42**, 3484 (1996).
16. Bird, R., Stewart, W., and Lightfoot, E., "Transport Phenomenon," Wiley, New York, 1960.
17. Torniainen, P. M., Chu, X., and Schmidt, L. D., *J. Catal.* **146**, 1 (1994).
18. Satterfield, C. N., "Heterogeneous Catalysis in Industrial Practice," McGraw–Hill, New York, 1991.
19. Perry, J., "Chemical Engineers' Handbook," McGraw-Hill, New York, 1963.
20. Le Bars, J., Vedrine, J. C., and Auroux, A., *Appl. Catal. A* **88**, 179 (1992).
21. Le Bars, J., Vendrine, J. C., Auroux, A., Pommier, B., and Pajonk, G. M., *J. Phys. Chem*. **96**, 2217 (1992).
22. Sweeting, T. R., Norris, D. A., Strom, L. A., and Morris, J. R., *Hi-Tech Ceramics* (1994).
23. Burch, R., and Crabb, E. M., *Appl. Catal. A* **100**, 111 (1993).
24. Morales, E., and Lunsford, J. H., *J. Catal.* **118**, 255 (1989).
25. Huff, M., and Schmidt, L., *Catal. Today* **21**, 113 (1994).
26. Dietz, A., Carlsson, A., and Schmidt, L., to be published.
27. Goetsch, D., and Schmidt, L., *Science* **271**, 1560 (1996).