Journal of Catalysis **195,** 376–382 (2000)
doi:10.1006/jcat.2000.2996, available online at http://www.idealibrary.com on IDEAL®

Isotopic Study of Ethanol Dehydrogenation over a Palladium Membrane

H. Amandusson,[1] L.-G. Ekedahl, and H. Dannetun

Forum Scientum and Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden

Received April 17, 2000; revised July 8, 2000; accepted July 8, 2000

Dehydrogenation of ethanol and the subsequent permeation of hydrogen through a 25-μm-thick palladium membrane has been studied. At 350°C, adsorbed ethanol will decompose on the surface. Initially, released hydrogen can permeate the membrane. In a continuous ethanol supply a carbonaceous layer will grow on the membrane surface, and eventually quench further permeation. If, however, oxygen is added to the ethanol supply, continuous oxidation of the decomposition products will occur, and the growth of the carbonaceous layer is suppressed. In this way a steady hydrogen permeation rate can be maintained. Experiments using isotopically labeled ethanol, CH_3CH_2OH, CH_3CH_2OD, CH_3CD_2OH, and CD_3CH_2OH, show that methyl hydrogen preferentially forms methane, and the hydroxyl hydrogen forms water, while it is the methylene hydrogen that is most likely to permeate the membrane.
© 2000 Academic Press

Key Words: **palladium; membrane; ethanol; hydrogen; dehydrogenation.**

---

1. INTRODUCTION

Catalytic membrane reactors have been gaining increasing interest lately (1). By combining the catalytic ability of a membrane surface with the selective permeation of certain species through the membrane, it is possible to remove products from a reversible reaction and thereby shift the reactions toward the product side. In this context, dehydrogenation and hydrogenation reactions on Pd membranes have been reviewed by Shu *et al.* (2). As an example of future applications, hydrogen permselective membranes could find use in fuel cells fed with alcohols. In this paper we study hydrogen permeation from ethanol, with the main focus on finding the reaction pathways of the hydrogen from the different functional groups.

We have previously studied hydrogen permeation from small alcohols and small hydrocarbons through palladium membranes. It is clear that hydrogen in methanol displays the largest hydrogen permeation probability. However, decomposition products will form a carbonaceous layer, which prevents further hydrogen permeation. In a continuous supply of methanol and oxygen, on the other hand, it is possible to produce a steady hydrogen permeation rate of the same order as that from pure hydrogen, since oxygen will prevent the formation of the carbonaceous layer. Furthermore, we have concluded that methyl hydrogen has a larger permeation probability than hydroxyl hydrogen (3). From unsaturated hydrocarbons no hydrogen permeation was obtained, even in the presence of oxygen (4). This information points to the necessity of an intact C–O bond in the reacting molecule in order to obtain hydrogen permeation.

Adsorption and decomposition of alcohols on Pd, especially methanol, but also ethanol and propanol, have received a great deal of interest. The results are thought to contribute to the industrially important reverse reaction, the catalytic formation of alcohols from synthesis gas. Synthesis of ethanol, e.g., is thought to require CO bond scission before hydrogenation to a methyl group can proceed (5). Ethanol has, however, been reported to form without CO bond scission if hydrocarbon species are added to a CO and hydrogen mixture on a palladium surface (6). Whether CO bond scission occurs during ethanol decomposition on palladium has been discussed in some contradictory papers (5, 7, 8).

Bowker *et al.* (5) report that the major pathway for ethanol decomposition on Pd(110) occurs via the surface ethoxy to a methyl group, carbon monoxide, and hydrogen adatoms. The methyl group either produces methane or can further decompose resulting in surface carbon. Methane production occurs with a high selectivity for temperatures below −23°C, while CH_3 decomposition mainly occurs above 77°C. Above 107°C no methane production was detected. When ethanol is adsorbed on oxygen-precovered Pd(110), the reaction pathways are not significantly changed, except for the production of water which leads to fewer hydrogen adatoms, i.e., a delay in the desorption of methane and hydrogen.

Bowker *et al.* (5) also found a minor reaction pathway, where C–O bond scission occurs, probably on defects. Shekhar and Barteau (7), on the other hand, report that no C–O bond scission occurs when ethanol is adsorbed on Pd(110) or Pd(111). They found methane, carbon monoxide, and hydrogen as the only decomposition products.

Davis and Barteau (9) found that the presence of oxygen on Pd(111) led to decomposition of ethanol into

---

[1] To whom correspondence should be addressed. Fax: +46-13-288969. E-mail: helam@ifm.liu.se.

0021-9517/00 $35.00

acetaldehyde (via dehydrogenation of surface ethoxy). Acetaldehyde either desorbed or oxidized to surface acetate, which either decomposed to adsorbed CO, H_2, and CH_4, or hydrogenated to acetic acid. On the clean Pd(111) surface, however, no formation of carboxylate species was found (9). Bowker *et al.* (5) also found that acetate can be formed in the presence of oxygen below −23°C but is decomposed to carbon monoxide and hydrogen at 127°C.

We have studied the continuous, steady-state decomposition of ethanol on a palladium membrane and the resulting hydrogen permeation through the membrane. A cosupply of oxygen is necessary to balance and reduce the formation of a contaminating layer of carbonaceous species and to keep a steady permeation rate. Our primary goal has been to study differences in permeation probability for differently bonded hydrogen atoms in the ethanol molecule and to identify the upstream decomposition products.

2. EXPERIMENTAL SET-UP

Gemini is a reactor designed for studies of chemical reactions involving catalytic membranes in the pressure range 1–1000 Torr (1 Torr = 133.3 N/m^2). The equipment is schematically shown in Fig. 1 and has been thoroughly described elsewhere (10). Since then, the two identical reactions cells (R1 and R2) have been modified and are now externally heated. The temperature is measured with a thermocouple in contact with the edge of the membrane. The catalytic membrane, in this case a 25-μm-thick palladium foil (Goodfellow, 99.95%), is mounted with VCR fittings as to separate the two cells. The active membrane surface area is approximately 11 mm in diameter.

Each reaction chamber has its own gas mixing system (up to five gases can be introduced on each side). The gas flows are controlled by mass flow regulators. The total chamber pressure can be regulated separately for each chamber. In order to monitor partial pressures of reactants, each reaction chamber is connected to a quadrupole mass spectrometer (QMS) via a quartz capillary leak (QC). With the capillary leak it is possible to keep a low pressure ($\sim 10^{-6}$ Torr) in the UHV chamber where the mass spectrometer is located. Any accidental leak rate between the two reaction chambers was several orders of magnitude below the smallest hydrogen permeation rate. It should be noted that there always is a certain background pressure in the chambers, giving rise to background signals in the spectra which is not compensated for.

During the experiments, the Pd membranes were continuously exposed to different combinations of ethanol, hydrogen, carbon monoxide, and oxygen. Gas-phase ethanol was produced from liquid, generated by flowing argon through an evaporator (see Fig. 1). Four types of isotope-labeled ethanol were used: CH_3CH_2OH (Kemetyl, pro analysis 99.5%), CH_3CH_2OD (ethyl alcohol-*d*; Aldrich, 99.5 atom% D), CH_3CD_2OH (ethyl-1,1-d_2 alcohol; Aldrich, 98 atom% D), and CD_3CH_2OH (ethyl-2,2,2-d_3 alcohol; Aldrich, 99 atom% D). Argon was used as carrier gas on both sides of the membrane. The total pressure in both reaction chambers was varied between 50–150 Torr and the membrane temperature between 150–450°C. The carbon monoxide was led through activated carbon prior to exposure in order to purify the gas from metal carbonyls.

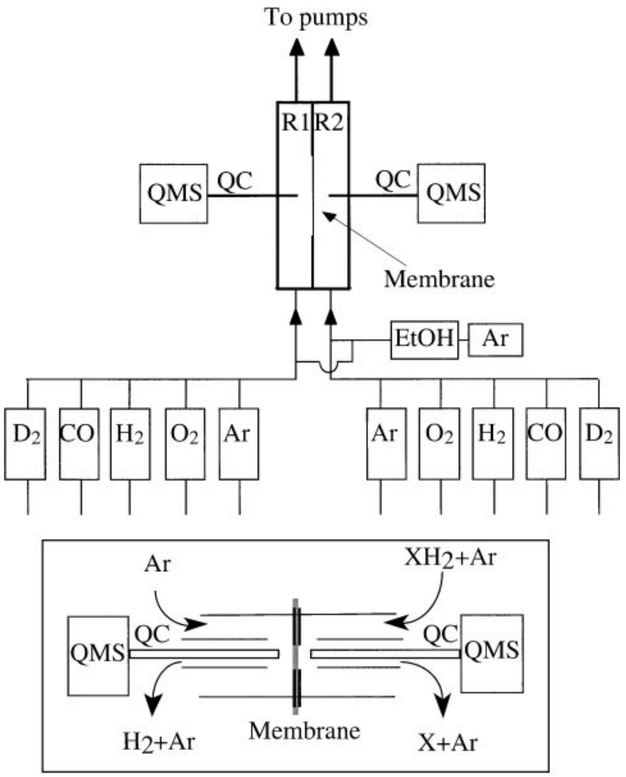

FIG. 1. Schematic layout of Gemini, the experimental set-up. R1 and R2 are the two reaction chambers, QC quartz capillaries, and QMS quadrupole mass spectrometers. Eleven mass flow controllers are available to regulate the flow of the gases (Ar, O_2, H_2, CO, and D_2). Gas-phase ethanol was produced from liquid, generated by flowing argon through an evaporator. The framed picture is a close-up of the reaction chambers.

Between experiments, the membrane was conditioned by alternating oxygen and hydrogen pulses at a temperature of 350°C. Experience from previous experiments in vacuum shows that, with this procedure, it is possible to obtain clean Pd surfaces within percentages of monolayers (11). In these studies reproducible results were always obtained after such a cleaning treatment.

3. RESULTS AND DISCUSSION

3.1. Hydrogen Permeation from Ethanol

When the palladium membrane is exposed to ethanol at 350°C, the alcohol mainly dissociates to methyl, carbon monoxide, and hydrogen. Initially, hydrogen can permeate

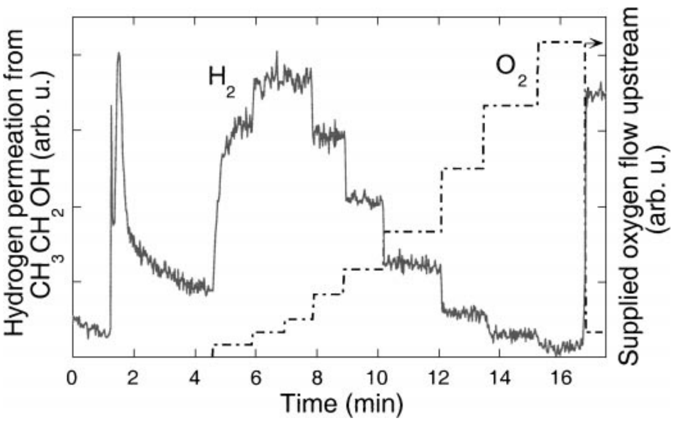

FIG. 2. Permeation of hydrogen from CH_3CH_2OH at 350°C. At $t=1$ min, 22 Torr ethanol is supplied upstream at a total pressure of 150 Torr. Oxygen is supplied upstream with stepwise increasing pressures from 1.5 Torr (introduced at $t=4.5$ min), up to 25 Torr.

the membrane but a carbon-dominating layer built up from the various species formed during the decomposition will eventually drastically decrease the rate of ethanol dissociation and the permeation will cease. When oxygen is added to the ethanol supply, two separate things occur (1). The built-up carbonaceous layer will transiently be oxidized, probably resulting in several different products (2). The CO group of the incoming ethanol molecule will mainly be oxidized to desorbing CO_2. In steady state, with a continuous oxygen/ethanol supply, the CO oxidation reaction to desorbing CO_2 and methane formation from the methyl group will dominate, balancing the formation rate of the permeating inhibiting carbonaceous layer.

Adsorbed oxygen, however, will react not only with the CO species, but also to some extent with adsorbed hydrogen. The oxygen/ethanol ratio is thus critical for the hydrogen permeation probability. In Fig. 2, the hydrogen permeation resulting from CH_3CH_2OH is shown. Ethanol is supplied upstream at $t=1$ min and it is clear that hydrogen is initially free to permeate the membrane. The carbonaceous layer built up on the upstream side, however, rapidly quenches the permeation. Introducing oxygen to the ethanol supply at $t=4.5$ min restores the permeation of hydrogen. The oxygen pressure is increased stepwise. With a low O_2 pressure, the efficiency of the oxidation process is insufficient, and thus a further increase of the oxygen pressure will promote permeation. With oxygen in excess, the water formation will increase upstream, leading to a reduced surface concentration of hydrogen and thus a smaller hydrogen permeation rate. Consequently, there exists an optimum oxygen/ethanol ratio where the permeation rate is maximized (which in this case occurs at an oxygen/ethanol ratio of 0.2 at an ethanol pressure of 20 Torr).

The hydrogen permeation rate produced at a certain ratio is very stable. Under a continuous ethanol and oxygen supply the permeation rate showed no decrease during exposures lasting for several hours. Hydrogen permeation through the membrane is also very fast (the theoretical time constant <0.01 s for the conditions in this study). An upstream supply of hydrogen will immediately cause a steady hydrogen pressure downstream. The downstream hydrogen/deuterium pressures are therefore representative of the chemistry on the upstream side of the membrane with no detectable time lag.

3.1.1. Reaction pathways for ethanol hydrogen. Isotopically labeled ethanol shows that, depending on their origin in the ethanol molecule, the hydrogen atoms experience different reaction pathways. In Figs. 3–5 the induced permeation rates of H_2, HD, or D_2 from CH_3CH_2OD, CH_3CD_2OH, and CD_3CH_2OH are displayed as a function of the oxygen/ethanol ratio. The oxygen pressure was increased stepwise, as in Fig. 2, in order to find the optimum conditions for permeation. For CH_3CH_2OD it is clear that hydrogen dominates the permeation. Small amounts of deuterium permeate at no or very low oxygen pressures (resulting also in a HD signal, Fig. 3), but decreases when the oxygen/ethanol ratio increases. For CH_3CD_2OH (Fig. 4), deuterium dominates the permeation and reaches a maximum for an oxygen/EtOH ratio of approximately 0.2. Some hydrogen permeates but hydrogen permeation decreases with oxygen supply. In the case of CD_3CH_2OH almost no deuterium permeates (Fig. 5). It is thus evident that differently bonded hydrogen atoms experience different reaction pathways on the palladium membrane surface.

The results show that, in the absence of, or at very small concentrations of, surface oxygen, hydroxyl hydrogen can permeate the membrane. With increasing oxygen pressure

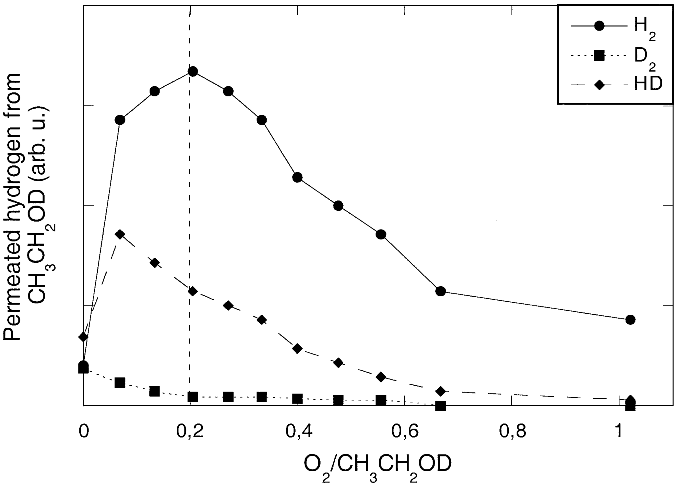

FIG. 3. Permeation of hydrogen from CH_3CH_2OD as a function of the supplied ratio of oxygen/ethanol pressure at 350°C. Mean values of the permeation rates during the steady-state condition are displayed. Note that the initial transient state on the clean membrane is not included. (The total pressure is 150 Torr; 14.75 ml/min EtOH and 0–25 ml/min oxygen is supplied.) The dotted line is drawn at the maximum permeation for the methylene hydrogen.

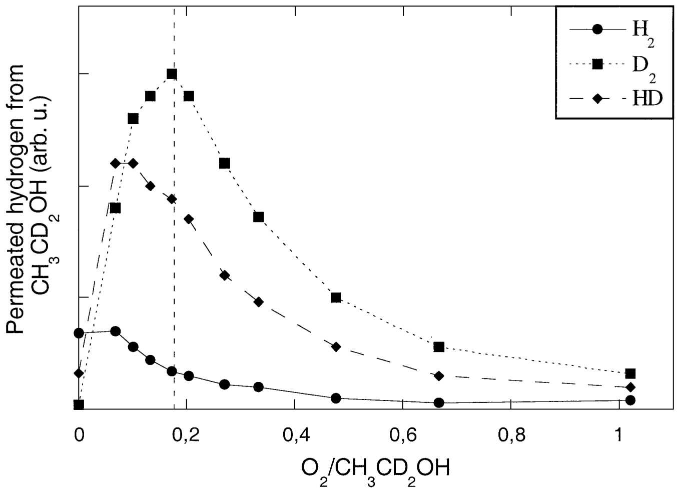

FIG. 4. Permeation of hydrogen from CH_3CD_2OH as a function of the supplied ratio of oxygen/ethanol pressure at 350°C. Mean values of the permeation rates during the steady-state condition are displayed. Note that the initial transient state on the clean membrane is not included. (The total pressure is 150 Torr; 14.75 ml/min EtOH and 0–20 ml/min oxygen is supplied.) The dotted line is drawn at maximum permeation for the methylene hydrogen.

the permeation of hydroxyl hydrogen declines rapidly. When oxygen is present on the surface, the hydroxyl hydrogen is directly displaced to adsorbed oxygen, forming OH and further on water. In this case, hydroxyl hydrogen never appears on the surface as free adsorbed hydrogen atoms, and is therefore not available for permeation. This has previously been demonstrated by Davis *et al.* (9), and is consistent with the results of this study. Thus, the conclusion is that the hydroxyl hydrogen (–OH) can permeate only for small O_2/EtOH ratios, but preferably forms water with increasing oxygen concentration.

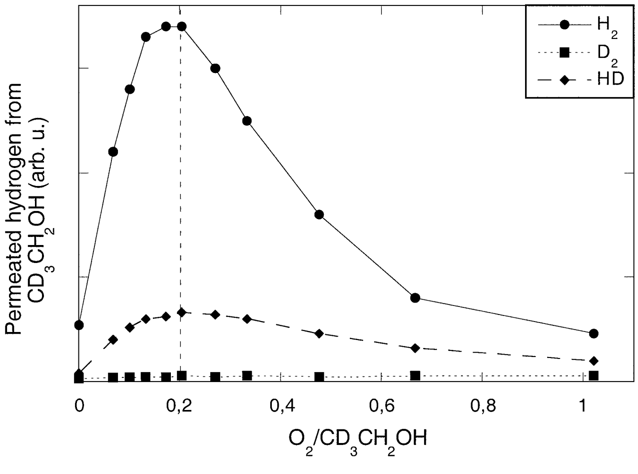

FIG. 5. Permeation of hydrogen from CD_3CH_2OH as a function of the supplied ratio of oxygen/ethanol pressure at 350°C. Mean values of the permeation rates during the steady-state condition are displayed. Note that the initial transient state on the clean membrane is not included. (The total pressure is 150 Torr; 14.75 ml/min EtOH and 0–25 ml/min oxygen is supplied.) The dotted line is drawn at maximum permeation for the methylene hydrogen.

The hydrogen atoms bonded to the methylene group ($-CH_2-$) are the hydrogen atoms that most likely permeate. This is also, as viewed by the QMS, the hydrogen that is most likely to desorb as hydrogen on the upstream side. From studies of upstream desorption products it is furthermore clear that it is the hydrogen from the methylene group that is responsible for the hydrogenation of the methyl group. The permeation of hydrogen from the $-CH_2-$ group initially increases as the oxygen supply is increased. The O_2/EtOH ratio is, however, delicate. When the oxygen pressure becomes too high, under these experimental conditions above 0.2 of the ethanol pressure, the hydrogen from the methylene group will also start to form water and permeation is reduced.

The hydrogen from the methyl group ($-CH_3$) mainly forms methane, most probably with one of the hydrogen atoms from the methylene group, at low or moderate oxygen pressures.

3.1.2. Upstream reaction products. Upstream desorption spectra were obtained for all isotopes of ethanol. By combining the results from the isotope studies a discussion of the origin of the different species can be made. As an example, the upstream desorption products from CH_3CH_2OH are presented in Fig. 6.

Hydrogen formation. The largest upstream desorption of hydrogen (as H_2, D_2, and/or HD) originates from the methylene group. The methyl hydrogen in turn produces

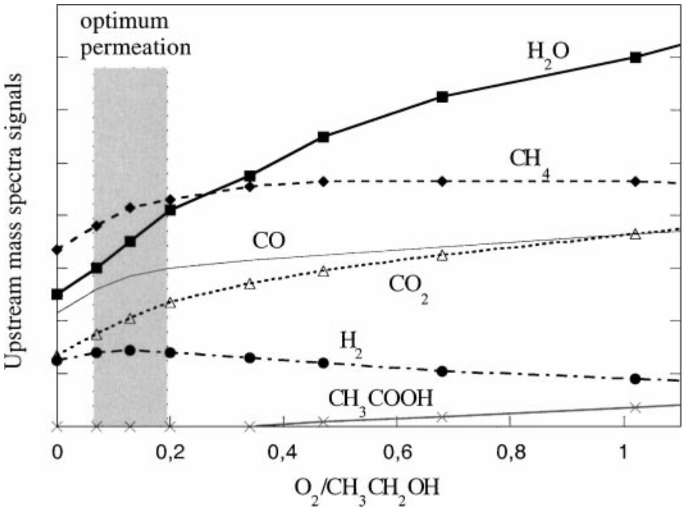

FIG. 6. Upstream decomposition products from CH_3CH_2OH for different oxygen/ethanol ratios. The total pressure is 150 Torr; 14.75 ml/min EtOH and 0–25 ml/min oxygen is supplied at 350°C. The mean values of the steady-state conditions are displayed. The marked area displays the condition for the highest hydrogen permeation rate. $m/e = 2$ is used for hydrogen, 18 for water, 28 for carbon monoxide, 44 for carbon monoxide, 15 for methane, and 60 for acetic acid (magnified 20 times). Note that no subtraction for cracking pattern or background has been made.

desorbing hydrogen to a greater extent than the hydroxyl hydrogen does. The desorption of hydroxyl hydrogen decreases immediately upon oxygen exposure, while the desorption of the methylene hydrogen increases with smaller oxygen pressures, but decreases when the optimum O_2/EtOH ratio is exceeded. This is also consistent with the conclusion that hydroxyl hydrogen and methyl hydrogen do not appear on the surface as atomically adsorbed hydrogen when adsorbed oxygen is present.

Water formation. When oxygen is introduced together with ethanol, the water production increases with increasing oxygen supply. Studies with isotopically labeled ethanol show that it is primarily hydroxyl hydrogen that is involved in the water formation. With oxygen in excess, water formation including the methylene hydrogen increases, leading to a decrease in permeation of that hydrogen.

Methane formation. When ethanol decomposes, the methyl groups forms methane together with a hydrogen atom preferentially originating from the methylene group. The methane production increases with increasing oxygen pressure to a certain level and then saturates at an O_2/EtOH ratio of approximately 0.4, i.e., at a larger ratio than the optimum permeation (see Fig. 6, where it should be noted that no background subtractions have been made). This result disagrees with Holroyd and Bowker (12), who found no methane production at temperatures above 107°C in TPD experiments. The upstream desorption rates of water and carbon dioxide, on the other hand, do not saturate but continuously increase as long as the oxygen supply is increased.

Cong *et al.* (13) found that if H_2 was coadsorbed with ethanol the production of the methane enhanced (as well as methanol formation) on Pt(331). We did not see such an effect. Adding hydrogen to the ethanol supply did not increase the methane production. The hydrogen desorption rate upstream and the hydrogen permeation rate, however, increased, which was expected as the partial pressure of hydrogen increased. The decomposition efficiency of ethanol in this study was on the whole reduced when hydrogen was cosupplied.

Acetic acid formation. When oxygen was in excess, acetic acid (CH_3COOH) was formed upstream. The acetic acid formation starts when water formation upstream starts to reduce the hydrogen surface concentration, and when the methane production saturates (see Fig. 6). This occurs at slightly higher oxygen pressures than for optimal permeation conditions. Coadsorption of CO will reduce the acetic acid formation, while coadsorption of hydrogen slightly enhances the formation.

The formation of acetic acid from ethanol on oxygen-precovered palladium surfaces has been observed before. Davis and Barteau (9) have found that on an oxygen-rich Pd(111) surface, ethanol dehydrogenated to acetaldehyde, which can be oxidized to surface acetate, and further on hydrogenate to acetic acid. This acetic acid was, however, reported to decompose at temperatures above 137°C. On clean Pd(111) no acetate was found (9). Holroyd and Bowker (12) also state that acetic acid is an intermediate in ethanol decomposition on oxygen-precovered Pd(110). In the membrane reactor used in this study, it is possible to observe the reactants and desorption products in the gas phase, but not the specific adsorbed surface species. However, since the desorbing products found in this study agree with the results from Davis and Barteau (9) and Holroyd and Bowker (12) we believe that it is likely that the formation of acetic acid proceeds via acetaldehyde and acetate intermediates.

3.1.3. Comparison with methanol and other hydrocarbons. In the ethanol molecule, only one of the two carbon atoms is bonded to oxygen. When ethanol dissociates on the membrane surface, at 350°C, in a non-oxygen-rich environment the C–C bond breaks. CO will easily oxidize, leaving its hydrogen available for permeation. The methyl group reacts with available hydrogen and forms desorbing methane and thus four out of six hydrogen atoms in the ethanol molecule are not available for permeation. With oxygen present on the surface, the hydroxyl hydrogen will immediately form OH, as discussed before, and is then not further available for permeation.

At 350°C we cannot of course rule out a minor decomposition pathway where the methyl group dissociates to adsorbed carbon and hydrogen. However, adsorbed carbon is not as easily oxidized as CO, and should in that case even more effectively than CO_{ad} block further ethanol adsorption. Previous studies of unsaturated hydrocarbons, which do dissociate completely, leaving C_{ad} on the Pd membrane surface, showed no evidence of hydrogen permeation during any mixture with oxygen (4). Since hydrogen permeation does proceed for ethanol in the presence of oxygen, the result from the hydrocarbon study supports the idea that the decomposition of the methyl group to C_{ad} is not significant.

A study similar to that described in this paper has previously been performed on methanol (3). The decomposition and reaction pathways are somewhat different from those of ethanol. In the methanol molecule the sole carbon atom is bonded to oxygen. The dehydrogenation of methanol, in the presence of oxygen, will result in adsorbed CO and hydrogen. The CO molecule is easily oxidized to CO_2, and consequently the surface is constantly regenerated under a continuous cosupply of oxygen and methanol. Since no hydroxyl hydrogen was detected on the downstream side with oxygen present, at most three out of the four methanol hydrogen atoms can theoretically, in a kinetic steady state, be available for permeation (which can be compared to one out of six in the ethanol case). As in the ethanol study, the hydroxyl hydrogen forms OH and water on the upstream side (3). Experimentally, the relative amount of permeated

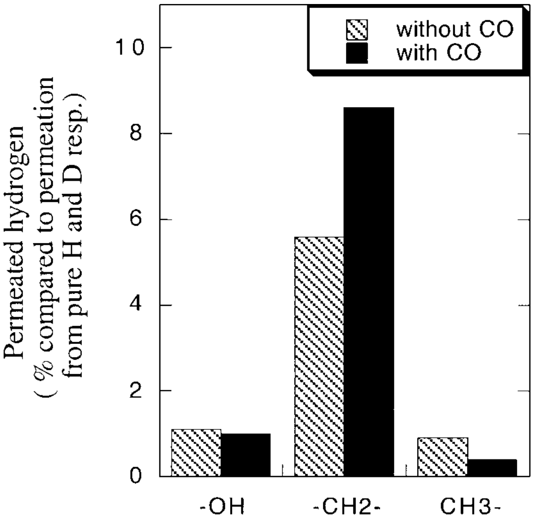

FIG. 7. Comparison of the maximum permeation for the different hydrogen atoms in ethanol with and without CO cosupplied to the EtOH + O_2 supply. (The total pressure is 150 Torr; 20 Torr EtOH is supplied, 4 Torr O_2 is supplied; without CO, and 13 Torr O_2 with 13 Torr CO.)

hydrogen from the ethanol molecule is smaller than that for methanol. The permeation probability of a hydrogen atom from ethanol was found to be 5–6 times lower than that from methanol, which is in fair agreement with the comparison of the theoretically available hydrogen, from a reaction scheme where hydroxyl hydrogen always forms water.

3.1.4. Additional observations. At temperatures lower than 350°C (150–250°C), no significant qualitative differences could be observed other than lower reaction rates.

At higher temperatures (450°C), the membrane will gradually reconstruct, leaving pores and cracks where oxygen can diffuse through the membrane.

It is also an experimental fact that if CO is added to the ethanol supply, the oxygen/ethanol ratio for maximum permeation is shifted upward; i.e., it is possible to add more oxygen without quenching the hydrogen permeation. (For example, optimum permeation conditions are obtained at an oxygen/ethanol ratio of 0.2 without CO and 0.69 with 12 Torr CO added, at an ethanol pressure of 20 Torr, in a total pressure of 150 Torr and a temperature of 350°C.) Ethanol will in this case be more efficiently decomposed, yielding a larger methane, carbon monoxide, and water production, while the upstream hydrogen desorption decreases. The hydrogen permeation will also increase, see Fig. 7. It is the permeation probability of the methylene hydrogen that increases, while the water formation with these hydrogen atoms decreases.

4. CONCLUSIONS

The dehydrogenation of ethanol and the subsequent permeation have been studied on a palladium membrane in a continuous ethanol supply. In order to maintain continuous hydrogen permeation, oxygen needs to be cosupplied with ethanol. Without oxygen the decomposition products will form a carbonaceous layer, which blocks ethanol dissociation and thus prevents hydrogen permeation.

Hydrogen cannot be extracted as efficiently from ethanol as from methanol. In ethanol at least four of the six hydrogen atoms are not available for permeation due to methane formation. Comparing the hydrogen permeation from ethanol, methanol, and small hydrocarbons leads to the conclusion that hydrogens bonded to a carbon atom in a C–O group are available for permeation, while hydrogen atoms bonded to a carbon atom without oxygen are not.

Under the conditions in this study, the efficiency of hydrogen permeation from ethanol is 5% compared to that of pure hydrogen, which can be compared to 25% for methanol compared to pure hydrogen.

It is possible to enhance the hydrogen permeation by adding CO to the EtOH + O_2 supply. It is the permeation probability of the hydrogen bonded to the methylene hydrogen that increases, while the water formation with this hydrogen atom decreases.

The differently bonded hydrogen atoms in an ethanol molecule experience different reaction pathways. It should be remembered that the results in this study were obtained under flowing conditions at steady state and pressures in the 10 Torr range. In light of this, it is interesting to note that the results do not contradict the models made from surface experiments in ultrahigh vacuum by Davis and Barteau (9), Holroyd and Bowker (12), or Bowker *et al.* (5).

- The methyl group will form methane with one of the methylene hydrogens.
- The hydroxyl hydrogen atoms can initially permeate the membrane or form water. With increasing oxygen pressure upstream, less of this hydrogen will permeate and more will form water. In fact, water is preferentially formed with the hydroxyl hydrogen.
- The methylene hydrogen displays the largest permeation and upstream desorption probabilities. This hydrogen is also provided to the methane production. With increasing oxygen pressure, the permeation first increases due to oxidation of the contaminating layer. However, the permeation will eventually decrease with increasing oxygen pressure due to water formation.
- At oxygen pressures exceeding that for optimum permeation conditions, a minor reaction pathway, including acetic acid formation, appears.

ACKNOWLEDGMENTS

Financial support of this work from the Swedish Foundation for Strategic Research (SSF), Swedish Natural Science Research Council (NFR), and the Swedish Research Council for Engineering Sciences (TFR) is gratefully acknowledged.

REFERENCES

1. Kikuchi, E., *CATTECH* March (1997).
2. Shu, J., Grandjean, B. P. A., Neste, A. V., and Kaliaguine, S., *Can. J. Chem. Eng.* **69**, 1036 (1991).
3. Amandusson, H., Ekedahl, L.-G., and Dannetun, H., *Surf. Sci.* **442**, 199 (1999).
4. Dannetun, H., Wilzen, L., and Petersson, L.-G., *Surf. Sci.* **357–358**, 804 (1996).
5. Bowker, M., Holroyd, R. P., Sharpe, R. G., Corneille, J. S., Francis, S. M., and Goodman, D. W., *Surf. Sci.* **370**, 113 (1997).
6. Farve, T. L. F., van der Lee, G., and Ponec, V., *J. Chem. Soc., Chem. Commun.* 230 (1985).
7. Shekhar, R., and Barteau, M. A., *Catal. Lett.* **31**, 221 (1995).
8. Holroyd, R. P., Bennett, R. A., Jones, I. Z., and Bowker, M., *J. Chem. Phys.* **110**, 8703 (1999).
9. Davis, J. L., and Barteau, M. A., *Surf. Sci.* **197**, 123 (1988).
10. Wilzén, L., and Petersson, L.-G., *Vacuum* **46**, 1237 (1995).
11. Eriksson, M., Linköping Studies in Science and Technology, Dissertation No. 504, 1997.
12. Holroyd, R. P., and Bowker, M., *Surf. Sci.* **377–379**, 786 (1997).
13. Cong, Y., van Spaendonk, V., and Masel, R. I., *Surf. Sci.* **385**, 246 (1997).