Catalysis Letters 6 (1990) 289–300

CO HYDROGENATION OVER NaY ENCAGED Pd CLUSTERS

F.A.P. CAVALCANTI, C. DOSSI, L.L. SHEU and W.M.H. SACHTLER

V.N. Ipatieff Laboratory, Center for Catalysis and Surface Science, Northwestern University, Evanston, Illinois, 60208, U.S.A.

Received 11 June 1990; accepted 23 August 1990

CO hydrogenation, methanol synthesis, hydrocarbon synthesis, hydrocarbon synthesis from methanol, palladium catalysts, zeolite supported palladium catalysts

CO hydrogenation has been studied over reduced Pd/NaY; a pronounced structure sensitivity was observed. Catalysts containing highly dispersed Pd clusters initially showed high selectivity towards CH_4, but as the Pd particles grew during the reaction the selectivity changed towards CH_3OH, CH_3OCH_3 and higher hydrocarbons. On catalysts initially containing large Pd particles, CH_3OH and CH_3OCH_3 were selectively formed from the start of the reaction. The results suggest that dissociative adsorption of CO is favored on very small Pd clusters leading to CH_4 formation. On larger Pd particles CH_3OH is formed; it is subsequently converted to CH_3OCH_3 and higher hydrocarbons on acid sites.

1. Introduction

CO hydrogenation to CH_3OH over Pd was first reported by Poutsma et al. [1] who attributed the activity and selectivity of Pd to its ability to adsorb CO non-dissociatively. Recently, Bell and Shustorovich [2] provided further support for this proposal through calculations based on zero-coverage activation barriers for elementary steps taking place on Pd (111). However, the mechanism of this reaction appears to be much more complex, as evidenced by the following experimental observations:

(1) Pd catalysts can produce CH_3OH and CH_4 simultaneously with varying selectivities [3–6]. Drastic changes in the yield of these products have been observed to occur as the reaction progresses [5,6].

(2) CH_4 and CH_3OH formation appear to be the result of independent processes [3–53].

(3) CH_3OH formation appears to be favored on large Pd particles, whereas CH_4 formation appears to predominate on small particles [3,4,7].

(4) Small Pd particles have been reported to dissociate chemisorbed CO upon heating to moderate temperatures, producing a carbon deposit that blocked CO

adsorption sites [3,8]. No major changes in the Pd particles morphology were observed during this process. Large Pd particles did not appear to be able to dissociate CO as easily.

Some observations are, however, apparently at variance with the above statements: Rieck and Bell [9] found that the turnover frequency for methanation increased with decreasing Pd dispersion for Pd/La_2O_3, whereas no effects of dispersion and morphology were found for Pd/SiO_2. For a fixed crystallite morphology, CH_3OH formation was found to be independent of Pd dispersion on both catalysts.

Fajula et al. [5] reported 100% selectivity towards CH_4 for CO hydrogenation over a Pd/NaY catalyst in a Berty-type recirculating reactor operated at 280°C and 15 atm. However, results of Kikuzono et al. [4] indicate that Pd/NaY is quite active and selective for CH_3OH production in a closed circulating system at 180°C and 0.6 atm.

The synthesis and structure of highly dispersed Pd clusters encaged in NaY zeolite has been extensively studied by our group [10,11]. When calcined at 500°C and reduced at 350°C, Pd/NaY was found to contain highly uniform Pd clusters entrapped in the zeolite cages. However, if the reduction was carried out at 500°C, Pd particles larger than the supercages were formed on the external surface or in voids (created by local collapse of the framework) of the zeolite.

In the present work, we take advantage of this ability to produce well defined Pd/NaY catalysts to explore some of the still unresolved issues concerning CO hydrogenation on Pd catalysts.

2. Experimental

2.1. CATALYSTS PREPARATION

Catalysts were prepared by ion exchange of Linde NaY (LZY-52) in a dilute aqueous solution of $[Pd(NH_3)_4](NO_3)_2$ (Strem Chemicals). The samples were then slowly heated in flowing O_2 to the desired calcination temperature (T_C). Reduction was conducted in flowing H_2 at a constant temperature (T_R) for t_R minutes. The metal loading and treatment conditions of each sample are denoted by $Pd_nNaY(T_C/T_R/t_R)$, in which n is the number of Pd atoms per unit cell of NaY. Catalyst preparation procedures have been detailed elsewhere [10,11].

2.2. REACTION STUDIES

CO hydrogenation at 220°C and 5 atm total pressure was carried out in a continuous-flow fixed bed reactor system (Max II Unit, Xytel Corp.). The total flow rate of the CO/H_2 mixture ($CO:H_2 = 1:2$) was 10 ml/min and 0.3 g of catalyst were used. The products were analyzed on-line with a HP 5890A GC equipped with a crosslinked methyl-silicon capillary column (i.d. = 0.2 mm, 50 m, He carrier) and FID.

CO hydrogenation was also studied at atmospheric pressure in a Pyrex glass fixed bed microflow reactor. The reaction temperature was 200°C; the reactant's total flow rate was 30 ml/min ($CO:H_2 = 1:2$), and 0.4 g of catalyst were used. Product analysis was carried out on-line with a HP 5890A GC fitted with a Porapak Q column (o.d. = 3 mm, 2 m, He carrier) and FID and TCD. Other reactions, which will be described later, were also carried out in this system. The transfer lines (stainless steel) to the GC's in both reaction systems were heated to 125°C.

2.3. FOURIER TRANSFORM INFRARED SPECTROSCOPY

Detailed procedures for sample preparation and data collection have been given previously [11]. The CO spectra were recorded after exposure of the catalysts to CO for 10 minutes at 25°C and purge in Ar for 30 minutes. A Nicolet 60SX single-beam FTIR spectrometer with a resolution of 1 cm^{-1} was used.

3. Results

3.1. REACTION STUDIES

3.1.1. Atmospheric pressure: The activity and selectivity for two consecutive CO hydrogenation periods over $Pd_7NaY(500/350/30)$ are shown in fig. 1. The carbon production for each reaction product is shown normalized to that for CH_4 at the beginning of the first reaction period, 71 μmole C/g.cat * hr. Fig. 1 shows that, during the first period, the selectivity and activity of the CO hydrogenation reaction changed drastically during the initial 3 hours of reaction. CH_4 production decreased by a factor of about 5, whereas CH_3OH and CH_3OCH_3 (DME) production steadily increased to values comparable to that of CH_4. The production of higher hydrocarbons (almost exclusively C_2H_6 with traces of C_3H_8) decreased rapidly during this period.

After a reaction period of 24 hours, the CO flow was turned off and the catalyst was exposed to a flow of H_2 for a period of 2.5 hours at 200°C. CH_4 production was detected during this period. Integration of the CH_4 production indicates that the amount of carbon removed from the surface was in the order of one monolayer for a Pd dispersion of 0.25.

Following this H_2 bracketing, another period of CO hydrogenation was carried out over the same catalyst. Fig. 1 shows that after 2 hours the catalyst returned to a level of activity and selectivity comparable to that at the end of the first CO hydrogenation period.

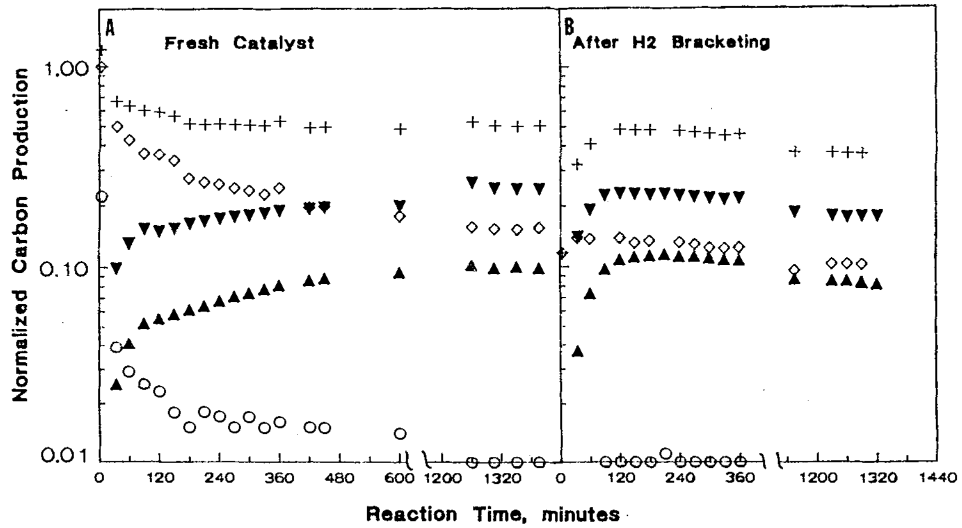

Fig. 1. CO hydrogenation over $Pd_7NaY(500/350/30)$. 200°C; 1 bar; $CO:H_2 = 1:2$; 4.5 l/g.cat * hr
(◇) CH_4; (○) C2+; (▲) DME; (▼) CH_3OH; (+) total
A – First CO hydrogenation period
B – Second CO hydrogenation period after H_2 bracketing.

CO disproportionation over $Pd_7NaY(500/350/30)$ was studied by exposing 0.4 g of the freshly reduced catalyst to CO in He (CO : He = 1 : 2, 30 ml/min) for 30 minutes at 200°C. CO_2 production was detected. Assuming that this was due to the Boudouard reaction, the amount of CO_2 detected in the gas phase indicates a deposition of about 0.1 of a monolayer of carbon on the catalyst surface. When CO hydrogenation was carried out over this CO-exposed catalyst, the initial CH_4 production corresponded to only 25% of the initial production from a "clean" catalyst. CH_3OH and DME were only barely detectable after 2.5 hours reaction. Exposure of the catalyst to a flow of H_2 for 1 hr at 350°C after CO hydrogenation for 1.5 hours removed about 0.7 of a monolayer of carbon. When a second CO hydrogenation was carried out over the CO-exposed catalyst after H_2 bracketing, the maximum CH_4 production was only 80% of that at the end of the first CO hydrogenation period. CH_3OH and DME were again only barely detectable after 5 hours reaction.

3.1.2. High pressure: The activity and selectivity for CO hydrogenation on $Pd_4NaY(500/350/20)$ and $Pd_4NaY(500/500/300)$ are shown in figs. 2 and 3, respectively. The metal dispersions for the freshly reduced catalysts measured by H_2 chemisorption were 0.78 and 0.05, respectively.

The results in fig. 2 are normalized with respect to the initial carbon production in CH_4, 250 μmole C/g.cat * hr. They show that the total activity on $Pd_4NaY(500/350/20)$ initially decreased and then remained constant without any major loss after 20 hours. While the selectivity for CH_4 formation decreased

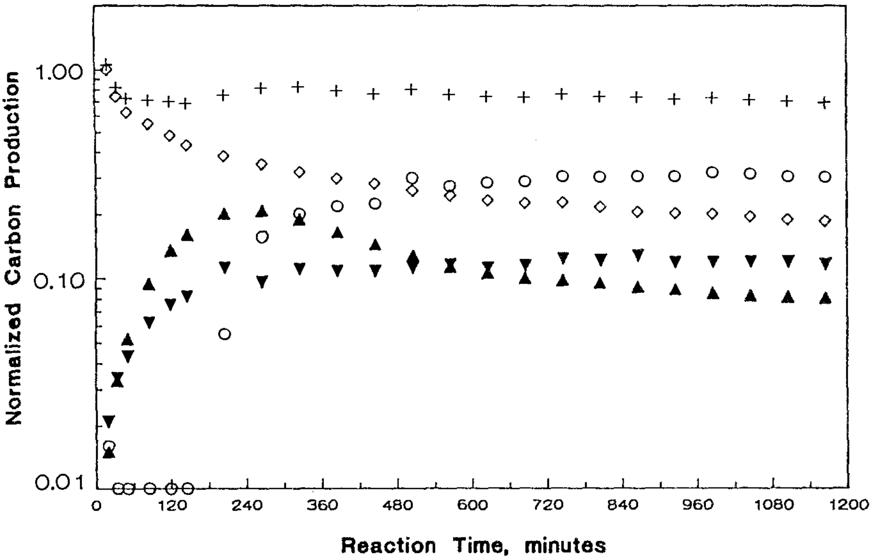

Fig. 2. CO hydrogenation over $Pd_4NaY(500/350/20)$. 220°C; 5 bar; $CO:H_2 = 1:2$; 2.0 l/g.cat * hr (◇) CH_4; (○) C2+; (▲) DME; (▼) CH_3OH; (+) total.

sharply during the first 3 hours of reaction, the selectivity to CH_3OH and DME increased greatly during this period. The rate of DME formation passed through a maximum at about 4 hours reaction and then decreased steadily. Formation of higher hydrocarbons with carbon number between 2 and 7 was also observed after an induction period of about 4 hours. These hydrocarbons consisted of at least 80% alkanes of carbon number greater than 3. Branched hydrocarbons

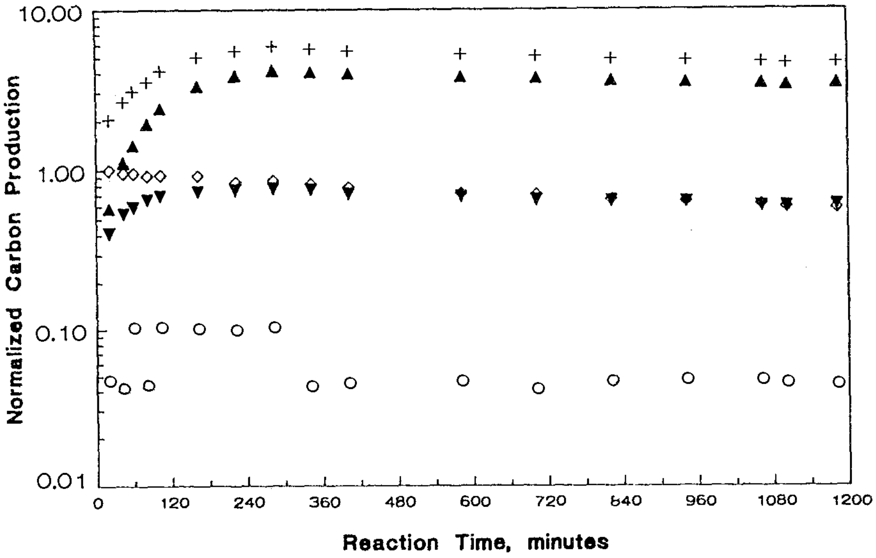

Fig. 3. CO hydrogenation over $Pd_4NaY(500/500/300)$. 220°C; 5 bar; $CO:H_2 = 1:2$; 2.0 l/g.cat * hr (◇) CH_4; (○) C2+; (▲) DME; (▼) CH_3OH; (+) total.

comprised more than 70% of the C_4, C_5, and C_6 fractions. No aromatic compounds were detected.

The catalyst sample reduced at 500°C showed an entirely different behavior as seen in fig. 3. The initial rate of CH_4 formation was 37 μmole C/g.cat * hr. The total activity initially increased and then remained constant. DME was the main product, while CH_4 and CH_3OH were formed in similar amounts. Only a very small amount of higher hydrocarbons was formed and these consisted almost entirely of C_2H_6 and C_3H_8. For comparable CO conversions, the activity of $Pd_4NaY(500/500/300)$ towards CH_4 formation was at the most half of that of $Pd_4NaY(500/350/20)$. CH_3OH production was about the same on both catalysts, whereas DME formation was 5 times larger for the catalyst reduced at 500°C.

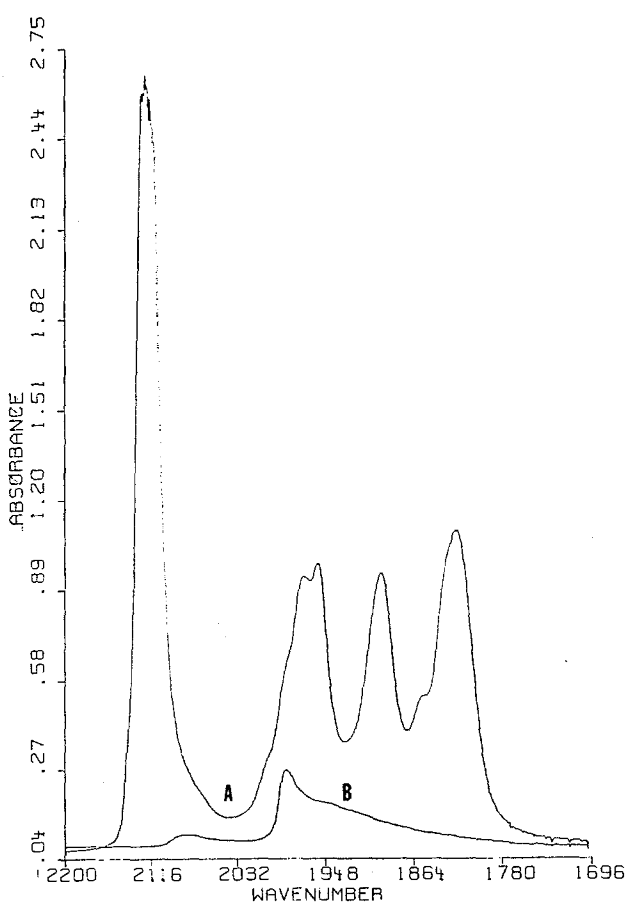

Fig. 4. Changes of CO/FTIR spectra of $Pd_4NaY(500/350/20)$. A before and B after reaction with CO/H_2 for 2 hours.

3.2. FTIR SPECTRA OF ADSORBED CO

FTIR spectra of CO adsorbed at 25°C on $Pd_4NaY(500/350/20)$ and $Pd_4NaY(500/500/300)$ prior to CO hydrogenation are shown in figs. 4A and 5A. The catalysts were then exposed to a flowing CO/H_2 mixture at 1 atm and 220°C for 2 hours to simulate the reaction conditions, which was followed by purging in Ar at 220°C for 2 hours. Analysis of the spectra of the two samples after Ar purging indicated that neither CO nor organic species, such as methoxy or methanol, remained adsorbed on the Pd particles. After flowing CO over the wafers and purging with Ar, the FTIR spectra of the adsorbed CO were recorded. They are shown in figs. 4B and 5B.

It is clear from fig. 4 that exposure of $Pd_4NaY(500/350/20)$ to the CO/H_2 mixture drastically changed the FTIR spectrum of adsorbed CO on the Pd particles from a highly structured spectrum exhibiting 6 sharp bands at 1823, 1900, 1956, 1965, 2114 and 2120 cm^{-1} to a spectrum containing only 2 broad

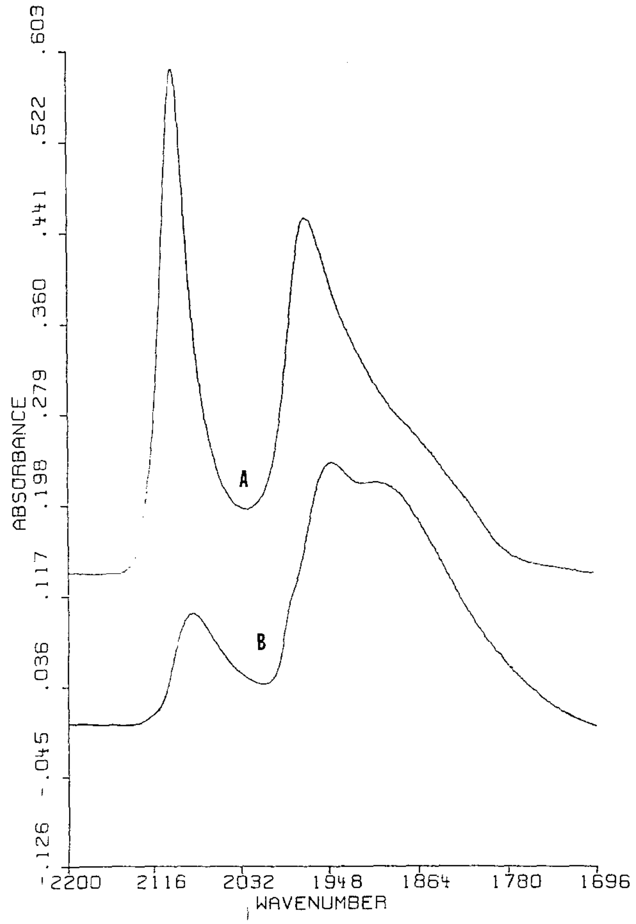

Fig. 5. Changes of CO/FTIR spectra of $Pd_4NaY(500/500/300)$. A before and B after reaction with CO/H_2 for 2 hours.

bands centered at about 1980 and 2080 cm^{-1}. In the case of $Pd_4NaY(500/500/300)$, exposure to the CO/H_2 mixture did not change the location of the CO absorption bands, but had a clear effect on their relative intensities, as seen in fig. 5.

4. Discussion

Figs. 1 and 2 show remarkable changes with time on-stream in the yield of the products obtained over the Pd/NaY catalysts reduced at 350°C. In order to rationalize these observations different causes might be considered.

The most trivial explanation which could be considered is that some of the products, in particular CH_3OH and DME, were preferentially adsorbed on the transfer lines between the reactor and the GC and/or on the zeolite support. This would lead to a false yield of these products at the start of the reaction. As mentioned earlier, the transfer lines for the high and low pressure systems were heated to 125°C in order to minimize this possibility. Additional evidence against such possibility is provided by figs. 1, 2 and 3. For example, even though the initial activity of $Pd_7NaY(500/350/30)$ was 3.5 times less than that of $Pd_4NaY(500/350/20)$, and even though both catalysts were tested in different systems and the reactions analyzed by different GC columns and methods, both catalysts displayed similar induction periods for CH_3OH and DME production. Also, the yield of CH_3OH, DME and higher hydrocarbons, products of vastly different physical properties, follow the same trend over both catalysts. Finally, although the initial activity of $Pd_4NaY(500/350/20)$ was 3.5 times larger than that of $Pd_4NaY(500/500/300)$, figs. 2 and 3 indicate that for the latter catalyst no major change in the yield of CH_3OH was observed. These observations rule out preferential CH_3OH and DME adsorption as a possible cause for the drastic changes with time on-stream in the yields of these products reported here.

The structure of Pd particles supported on NaY has been obtained from FTIR of adsorbed CO [11]: highly structured spectra suggest the existence of uniform $Pd_{13}(CO)_x$ clusters, while CO adsorbed on large particles (20 Å or larger) gives rise to a broad band in the multiply bonded CO regime, below 2000 cm^{-1}. The FTIR spectrum shown in fig. 4A for $Pd_4NaY(500/350/20)$ suggests that, prior to CO hydrogenation, the majority of the Pd is present as highly dispersed, uniform Pd clusters. After reaction with CO/H_2, fig. 4B, a broad band in the multiply bonded CO regime (< 2000 cm^{-1}) and a small band in the linearly bonded CO regime (> 2000 cm^{-1}), typical of large Pd particles, appear. CO-induced Pd particle growth in Pd/NaY has also been confirmed by EXAFS [12].

With $Pd_4NaY(500/350/20)$ and $Pd_7NaY(500/350/30)$, initially containing very small Pd clusters, the initial yield was almost exclusively CH_4. Remarkably, the CH_4 yield decreased sharply on both catalysts during the first 3 hours of reaction, while at the same time the formation of CH_3OH and DME increased drastically. Simultaneously, the Pd particles increase in size as indicated by CO/FTIR. This suggests that CO hydrogenation on Pd/NaY is strongly structure sensitive. CH_4 formation appears to be favored on small Pd particles, while CH_3OH and DME formation is favored on large Pd particles. This suggestion is further supported by the results obtained for the Pd_4NaY(500/500/300) catalyst and for the second CO hydrogenation period on Pd_7NaY (500/350/30). For both cases, where large Pd particles are present from the beginning of the reaction, the products rapidly reached a steady-state composition in which CH_3OH and DME predominated over CH_4.

An alternative explanation for the yield changes with time on-stream might involve a promoter effect by the Na^+ ions present in the zeolite. As the Pd particles grow, the ratio of Na^+ to Pd surface atoms could change. Although there are reports [13] which suggest a promoter effect by NaO_x on Cu catalysts for CH_3OH synthesis, the possibility of Na promotion on Pd catalysts is by no means well established. For example, the results of Lunsford and co-workers [14] indicate that impregnating "unpromoted" Pd/SiO_2 ($Na/Pd = 0.056$) with Na_2CO_3 to obtain $Na/Pd = 2.0$ had no significant effect on the selectivity or activity of the catalyst for CH_3OH synthesis. In another publication [5], the same group found that a Pd/NaY catalyst was neither more active nor more selective for CH_3OH synthesis than PdHY or any of the SiO_2-supported Pd catalysts tested. Tamaru and co-workers [4] proposed a promoting effect for Na, but their results showed that impregnation with NaCl or NaOH of catalysts prepared from Na-free Pd precursors did not result in an enhancement of CH_3OH synthesis. When discussing the present Pd/NaY catalysts it is important to realize that the Na^+ ions in an intact zeolite must stay inside cages to neutralize the negative charge of the lattice, but that the Pd particles can be formed on the zeolite's external surface. A comparison of Pd_4NaY(500/350/20) with Pd_4NaY(500/500/30) after 20 hours reaction is, therefore, relevant. While the total activity of both catalysts is identical, the latter was significantly more selective to CH_3OH and CH_3OH-derived products than the former. This observation makes Ha promotion unlikely since a large portion of the Pd particles in Pd_4NaY(500/500/300) is located at the exterior of the. zeolite crystallites where the availability of Na^+ for promotion is low. We, therefore, conclude on the basis of our data and that of other workers that Na promotion is unlikely to be the cause of the changes in products yield reported here.

The results of the CO disproportionation over Pd_7NaY(500/350/30) indicate that small Pd particles readily dissociate CO at 200°C. Even though less than a monolayer of carbon was deposited, it substantially inhibited the catalyst's activity towards CO hydrogenation. This is consistent with previous reports [3,8] that CO disproportionation on small Pd particles suppresses further CO chemisorption.

The large yield of DME over all Pd/NaY catalysts can be attributed to the secondary dehydration of CH_3OH on acid sites of the zeolite support. These acid sites are formed during the reduction of the Pd^{2+} ions. Fujimoto et al. [15] studied the reactivity of CH_3OH formed during CO hydrogenation over mixtures of Pd/SiO_2 and various zeolites. They showed that acid zeolites can convert CH_3OH formed on the Pd/SiO_2 catalyst to DME and hydrocarbons, as in the MOBIL process [16]. We have confirmed this observation by reacting a mixture of $He:H_2:CH_3OH(80:16:4)$ over freshly reduced $Pd_7NaY(500/350/30)$ at 200°C and 1 atm for 18 hours. For these conditions, a maximum of 1% of the CH_3OH was converted to CH_4, while conversion to DME varied from 30 to 40%. No higher hydrocarbons were formed under conditions.

The large selectivity towards higher hydrocarbons formation displayed by the $Pd_4NaY(500/350/20)$ catalyst is very interesting. The carbon number distribution, as well as the highly branched nature of the hydrocarbons formed, clearly show a reaction pathway distinct from the traditional Fischer-Tropsch chain growth. Apparently, the C3 + products are formed via the stepwise dehydration of CH_3OH to DME and further to hydrocarbons as in the MOBIL process over HZSM-5 [16]. This is further supported by the observation that the yield DME, fig. 2, went through a maximum as the formation of higher hydrocarbons started to increase. The reason why the catalyst reduced at 350°C is more active in the production of higher hydrocarbons than the one reduced at 500°C deserves further study. Ono and Mori [17] reported that the formation of DME from CH_3OH on acidic zeolites proceeds on weak acid sites, while hydrocarbon formation requires stronger acid sites. It appears conceivable that the interaction of protons with Pd_{13} clusters in $Pd_4NaY(500/350/20)$ leads to the formation of new, active acid sites which convert DME to higher hydrocarbons.

5. Conclusions

The hydrogenation of CO over Pd/NaY is strongly sensitive to the size of the Pd particles. On highly dispersed Pd, CO is initially chemisorbed dissociatively and CH_4 is selectively formed. When the small Pd clusters sinter forming large Pd particles, the selectivity changes drastically towards CH_3OH and its dehydration products. On those catalysts which contain large Pd particles, CH_3OH and DME are selectively formed from the start of the reaction.

At 220°C and 5 atm, the Pd/NaY catalyst reduced at low temperature is very selective towards the formation of higher, highly branched, alkanes. This opens up the possibility of using a single dual-function (acid + metal) catalyst for converting CO/H_2 mixtures to hydrocarbons via the intermediate formation of CH_3OH and DME, avoiding the limitations of the conventional Fischer-Tropsch synthesis.

Acknowledgement

Support of this research by grant no. CTS 89 11184 from the National Science Foundation is gratefully acknowledged.

References

[1] M.L. Poutsma, L.F. Elek, P.A. Ibarbia, A.P. Risch and J.A. Rabo, J. Catal. 52 (1978) 157.
[2] A.T. Bell and E. Shustorovich, J. Catal. 121 (1990) 1.
[3] S. Ichikawa, H. Poppa and M. Boudart, J. Catal. 91 (1985) 1.
[4] Y. Kikuzono, S. Kagami, S. Naito, T. Onishi and K. Tamaru, Faraday Disc., Chem. Soc. 72 (1981) 135.
[5] F. Fajula, R.G. Anthony and J.H. Lunsford, J. Catal. 73 (1982) 237.
[6] J.M. Driessen, E.K. Poels, J.P. Hindermann and V. Ponec, J. Catal. 82 (1983) 26.
[7] K.P. Kelly, T. Tatsumi, T. Uematsu, D.J. Driscoll and J.H. Lunsford, J. Catal. 101 (1986) 396.
[8] D.L. Doering, H. Poppa and J.T. Dickinson, J. Catal. 73 (1982) 104.
[9] a. J.S. Rieck and A.T. Bell, J. Catal. 103 (1987) 46;
b. J.S. Rieck and A.T. Bell, J. Catal. 90 (1985) 205.
[10] a. S.T. Homeyer and W.M.H. Sachtler, J. Catal. 118 (1989) 266;
b. S.T. Homeyer and W.M.H. Sachtler, J. Catal. 117 (1989) 91.
[11] a. L.L. Sheu, H. Knözinger and W.M.H. Sachtler, Catal. Lett. 2 (1989) 129;
b. L.L. Sheu, H. Knozinger and W.M.H. Sachtler, J. Am. Chem. Soc. 111 (1989) 8125.
[12] Z. Zhang, H. Chen, L.L. Sheu and W.M.H. Sachtler, J. Catal., in press.
[13] a. J.A. Brown Bourzutschky, N. Homs and A.T. Bell, J. Catal. 124 (1990) 52.
b. J.A. Brown Bourzutschky, N. Homs and A.T. Bell, J. Catal. 124 (1990) 73.
[14] K.P. Kelly, T. Tatsumi, T. Uematsu, D.J. Driscoll and J.H. Lunsford, J. Catal. 101 (1986) 396.
[15] a. K. Fujimoto, H. Saima and H.-O. Tominaga, J. Catal. 94 (1985) 16;
b. K. Fujimoto, Y. Kudo and H.-O. Tominaga, J. Catal. 87 (1984) 136.
[16] a. C.D. Chang and A. Silvestri, J. Catal. 47 (1977) 249;
b. S.L. Meisel, J.P. McCullough, C.H. Lechthaler and P.B. Weisz, Chemtech 6 (1976) 86.
[17] Y. Ono and T. Mori, J. Chem. Soc., Faraday Trans. I, 77 (1981) 2209.