JOURNAL OF CATALYSIS **175,** 302–311 (1998)
ARTICLE NO. CA981996

Basic Metal Oxides as Co-Catalysts in the Conversion of Synthesis Gas to Methanol on Supported Palladium Catalysts

A. Gotti and R. Prins[1]

Laboratory of Technical Chemistry, Swiss Federal Institute of Technology (ETH), 8092 Zürich, Switzerland

Received September 25, 1997; revised December 11, 1997; accepted December 11, 1997

The catalytic behavior of Pd catalysts supported on ultrapure silica and promoted with basic metal oxides was investigated in the hydrogenation of CO and CO_2 to methanol at high pressure. In contrast to previous claims, Pd on very pure silica produced hardly any methanol from CO and H_2 or CO_2 and H_2, while doping with basic additives led to a high activity. Molecular adsorption of CO or CO_2 and the availability of activated hydrogen are not sufficient to form methanol; basic metal oxides are needed to give Pd a high methanol activity. The promoting effect on the silica-supported Pd catalysts and the absence of a promoting effect for alumina-supported Pd catalysts suggest that the basic oxide additives must be close to or in contact with the Pd particles to be effective in methanol synthesis. The rate enhancements for methanol formation of the metal oxides followed a volcano curve when plotted as a function of the metal ion electronegativity, with a maximum for metal oxides with a moderate basic nature. Calcium and lanthanum were best for CO hydrogenation, and barium and lanthanum were best for CO_2 hydrogenation. In contrast to Cu/ZnO, the methanol activity of $Ca/Pd/SiO_2$ increased with increasing CO content in a $CO–CO_2–H_2$ mixture, suggesting that CO rather than CO_2 is the main carbon source for methanol. © 1998 Academic Press

INTRODUCTION

For many years, supported palladium catalysts have been claimed to be good catalysts for the production of methanol (1, 2). Whereas Rh is a metal on the borderline between adsorbing CO dissociatively and associatively, Pd is hardly capable of dissociating CO (3, 4). Thus, Boudouard CO disproportionation studies have shown that CO adsorption on Pd at 573 K is predominantly nondissociative (5). This explains why Pd, Pt, and Ir rank low in a comparison of group VIII metals for hydrogenation of CO to CH_4 at 0.1 MPa (6).

Poutsma *et al.* (2) reported that the same Pd, Pt, and Ir catalysts, supported on Davison grade 57 SiO_2, transform synthesis gas almost quantitatively into methanol when operated in the suitable thermodynamic regime. They ascribed the high activities and selectivities to the ability of Pd, Pt, and Ir to chemisorb CO associatively and hydrogenate it to CH_3OH, and to their inability to chemisorb CO dissociatively. Subsequent work of Fajula *et al.* (7) on Pd supported on SiO_2 and Y zeolites demonstrated, however, that selectivity and activity depended on the support. Over acidic Pd/Y and over Pd/SiO_2, prepared from Davison grade 01 silica, mainly methane was produced, while over Pd/SiO_2 supported on a Davison grade 57 SiO_2 methanol was the main product. On the other hand, only very little methanol was observed when reacting synthesis gas over unsupported Pd, e.g. Pd black (8).

These observations suggest that impurities in the support, which can be transferred easily to the metal surface during catalyst preparation or reaction, may influence catalyst performance (9, 10). Indeed, it was claimed in patents that basic oxide additives significantly improve the hydrogenation of CO to methanol (11), and studies with Pd/SiO_2 catalysts promoted by alkaline earth oxides, iron oxide, and La_2O_3, as well as studies with Pd catalysts directly supported on such basic oxides, indicated high methanol selectivities at low and normal pressure, be it with low yields (4, 8, 12–14).

Therefore, the present study investigates the catalytic properties of Pd catalysts supported on SiO_2 in the conversion of synthesis gas. In contrast with previous studies, the silica was synthesized in a very pure form to avoid unintentional contamination which could affect the catalytic properties; the experiments were carried out under realistic conditions: a continuous flow reactor instead of a closed circulating system, high instead of (sub)ambient pressure, and 24 h activity tests to check steady state properties and catalyst stability.

The catalytic behavior of Pd supported on ultra pure silica in the hydrogenation of CO was compared with the catalytic performance of Rh/SiO_2. The effect of residual anions was studied by analyzing the properties of Pd/SiO_2 catalysts prepared from chloride and nitrate salts. Ca-doped Pd catalysts, with increasing additive to metal ratios, and Pd/SiO_2 catalysts doped with several metal oxides were employed to investigate the role of basic metal oxides in the formation of methanol from synthesis gas. To better understand the role

---

[1] To whom correspondence should be addressed. Tel.: 41-1-6325490. Fax: 41-1-6321162. E-mail: prins@tech.chem.ethz.ch.

0021-9517/98 $25.00

of CO and CO_2 and their interconversion in the water–gas shift reaction during the methanol synthesis, the properties of the catalysts in the hydrogenation of CO, CO_2, and CO–CO_2 mixtures were studied.

EXPERIMENTAL

Catalyst Preparation

Ultrapure silica, prepared by hydrolysis of tetraethoxysilane (15), was ground, sieved to a 250–300 μm size fraction, and stored in a desiccator until use. Pd/SiO_2 catalysts were prepared by pore volume impregnation of this impurity-free SiO_2 with an aqueous solution of $Pd(NH_3)_4(NO_3)_2$ (Johnson Matthey). The catalyst precursors were dried at 393 K (heating rate 60 $K \cdot h^{-1}$) for 16 h and calcined in flowing air at 723 K (heating rate 300 $K \cdot h^{-1}$) for 2 h. The Pd loading was 4.5 wt% in all cases. $Ca/Pd/SiO_2$ catalysts with Ca/Pd ratios between 0.04 and 0.33 were prepared by impregnating these Pd/SiO_2 catalysts with a $Ca(NO_3)_2$ solution, and calcining and drying them as described above. Similarly, two $Ca/Pd/SiO_2$ catalysts were prepared from $Pd(NO_3)_2$ and $PdCl_2$ (Johnson Matthey) solutions with a Pd loading of 4.5 wt% and a Ca/Pd = 0.04 ratio.

$X/Pd/SiO_2$ catalysts (X = Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Mn, Zn, La) with an atomic ratio X/Pd = 0.125 were prepared by impregnation of a calcined Pd/SiO_2 precursor (prepared from $Pd(NH_3)_4(NO_3)_2$) with nitrate solutions of the additives. The catalysts were dried and calcined as described above for the other catalysts.

Pd/Al_2O_3 was obtained by pore volume impregnation of a commercial γ-alumina (Condea, 250–300 μm, 226 m^2/g, 0.51 mL/g) with an aqueous $Pd(NH_3)_4(NO_3)_2$ (Johnson Matthey) solution. The catalyst precursor was dried and calcined as described for the Pd/SiO_2 catalyst. The Pd loading was 3.0 wt%. A $Ca/Pd/Al_2O_3$ catalyst with Ca/Pd = 0.2 was prepared by impregnating the calcined Pd/Al_2O_3 catalyst with a $Ca(NO_3)_2$ solution and drying and calcining as described above. For comparison, a Rh/SiO_2 catalyst was prepared as described in (16).

To prevent the uptake of alkali and alkaline earth metal cations from glass, the preparation of the supports and the subsequent catalyst preparation were always carried out in polyethylene equipment which had been washed previously with 5% boric acid and rinsed with water, distilled twice.

Characterization

Surface area, pore volume, and pore size distribution of the self-made ultrapure SiO_2 support were obtained from nitrogen adsorption and desorption isotherms at 77 K and at equilibrium pressures between 0.5 and 100 kPa. Hydrogen chemisorption was performed on catalysts (typically containing 1–2 mg of Pd) reduced in flowing H_2 at 723 K (300 $K \cdot h^{-1}$) for 1 h and evacuated at 10^{-2} Pa for 1 h. Because the formation of the β-hydride phase will affect the results, the backsorption method was applied (16), and the H/Pd values were obtained by subtracting the backsorption isotherm from the total adsorption isotherm $[H_{irr}/Pd = (H_{tot} - H_{rev})/Pd]$.

TPR measurements were carried out on catalysts containing 25–55 μmol of reducible species with 5% H_2 in Ar at a flow rate of 0.183 $cm^3 \cdot s^{-1}$ from 180 to 980 K with a temperature ramp of 10 $K \cdot min^{-1}$. After cooling in H_2/Ar to 180 K the flow was switched to Ar, and a second switch peak was recorded by switching back to 5% H_2/Ar. The comparison of the two peaks revealed the hydrogen uptake hidden under the first switch peak (17).

Catalyst Testing

Synthesis gas conversion was performed in a steel reactor equipped with an internal quartz reactor to avoid contamination of the catalyst with Fe, Ni, or Cr formed from metal carbonyls by the reaction of the steel with CO; for the same reason, a γ-Al_2O_3 trap upstream of the catalyst bed was used to adsorb such metal carbonyls. About 300 mg of catalyst precursor was reduced in a flow of pure hydrogen at 723 K and 0.1 MPa for 1 h. The catalyst amount was chosen in order to keep the conversion between 0.1% (necessary for accurate product analysis) and 5% (differential conditions). After cooling to reaction temperature, the hydrogen pressure was increased to working pressure, and CO or CO_2 was added stepwise to the feed. Unless otherwise stated, the Pd catalysts were tested at 553 K, 2.5 MPa, $H_2/CO = 2$ ($flow_{feed} = 0.11\ mol \cdot h^{-1}$), $H_2/CO_2 = 3$ ($flow_{feed} = 0.15\ mol \cdot h^{-1}$), and at a space velocity of 770 $mol_{feed} \cdot h^{-1}/mol_{Pd}$. The Rh/SiO_2 catalyst was tested at 553 K, 4 MPa, $H_2/CO = 3$, and SV = $10^4\ mol_{feed} \cdot h^{-1}/mol_{Rh}$ (16). The experiments were generally carried out for 24 h on stream. The reactor effluent was analyzed every 30 min by a computer-interfaced on-line GC. The product activities and selectivities were summarized in four main classes: CH_4, C_{2+} (paraffins and olefins with $n \geq 2$), $C_{1\text{-oxo}}$ (methanol and dimethyl ether), and $C_{2\text{-oxo}}$ (acetaldehyde and ethanol).

RESULTS

Catalyst Characterization

The BET surface area (534 m^2/g), pore volume (1.39 mL/g), and pore size distribution (mainly in the 80–175 Å range) of the SiO_2 support, prepared by hydrolysis of tetraethoxysilane, are very similar to those of commercially available SiO_2 supports, whereas the purity is very much higher (AAS and ICP measurements showed that the ultrapure silica contained impurities in the sub-ppm level only).

The TPR profile of a Pd/SiO_2 catalyst prepared from $PdCl_2$ showed a peak at 400 K with a half-width of 70 K. No hydrogen consumption was observed above 650 K, and the calculated H_2/M value near 1.0 indicated full conversion of

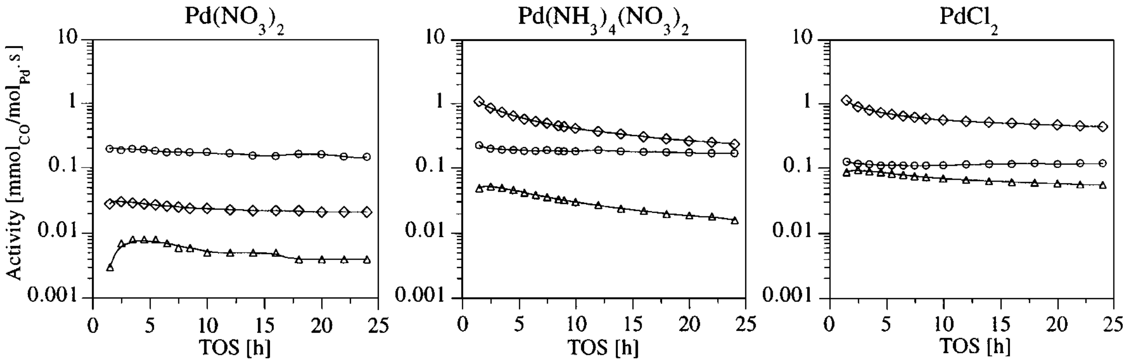


FIG. 1. Product activities in the hydrogenation of CO over Pd/SiO$_2$ prepared from different Pd salts. (◇) CH$_4$, (△) C$_{2+}$, (○) C$_{1\text{-oxo}}$.

Pd^{2+} cations to Pd^0 clusters. Therefore, reduction at 723 K for 1 h in flowing hydrogen, as applied before catalyst testing, is sufficient to completely reduce the supported Pd catalysts.

Although the promoters were added as a nitrate salt during catalyst preparation, the subsequent calcination in air at 723 K will have transformed them into oxides. An XPS measurement showed that after subsequent reduction at 723 K in hydrogen, calcium was present in the +2 oxidation state. Therefore, it is assumed that the promoters described in this study (perhaps with the exception of Zn, see Discussion) were present as metal oxides and/or (surface) metal silicates during reaction.

CO Hydrogenation over Pd/SiO$_2$ and Ca/Pd/SiO$_2$

The product activities in the CO hydrogenation over the Pd/SiO$_2$ catalysts made from Pd(NO$_3$)$_2$, Pd(NH$_3$)$_4$(NO$_3$)$_2$, and PdCl$_2$ as a function of reaction time (TOS = time on stream) are presented in Fig. 1. Because Pd can hardly dissociate CO, the total activity of the Pd/SiO$_2$ catalysts was almost 2 orders of magnitude smaller than that of Rh/SiO$_2$ (16), and the product distribution was limited to methane, trace amounts of ethane and propane, and C$_{1\text{-oxo}}$ products (methanol and dimethyl ether); acetaldehyde and ethanol were not formed. The three Pd/SiO$_2$ catalysts had a methanol activity about as low as Rh/SiO$_2$, indicating that Pd catalysts supported on impurity-free SiO$_2$ are not particularly efficient in producing methanol, in contrast to claims made by Poutsma *et al.* (2).

The Pd salt had an influence on the properties of the resulting Pd/SiO$_2$ catalyst. Catalysts prepared from PdCl$_2$ and Pd(NH$_3$)$_4$(NO$_3$)$_2$ had a higher hydrocarbon activity than the catalyst prepared from Pd(NO$_3$)$_2$, whereas all catalysts had a similarly low methanol production (Fig. 1). Since only traces of chlorine were detected in the Pd/SiO$_2$ catalyst prepared from PdCl$_2$ after reduction (Cl/Pd = 3.5×10^{-4}), and no nitrogen was detected in the catalysts prepared from the nitrate salts, the Pd salt anion cannot influence the catalysis. It has an indirect effect, however, through its influence on the final metal dispersion. The H$_{irr}$/Pd values for the catalysts obtained from Pd(NH$_3$)$_4$(NO$_3$)$_2$, PdCl$_2$, and Pd(NO$_3$)$_2$ were 0.28, 0.30, and 0.02, corresponding to average particle diameters of 35, 32, and 550 Å, respectively. CO dissociation is known to be favored on small Pd particles (18, 19), and therefore the Pd particles obtained from Pd(NH$_3$)$_4$(NO$_3$)$_2$ and PdCl$_2$ had the highest hydrocarbon activity.

Doping of the Pd/SiO$_2$ catalysts with 1000 ppm (molar) Ca resulted in a strong decrease in the hydrocarbon formation due to the suppression of the CO dissociation and a higher methanol production (Fig. 2). The Ca-doped

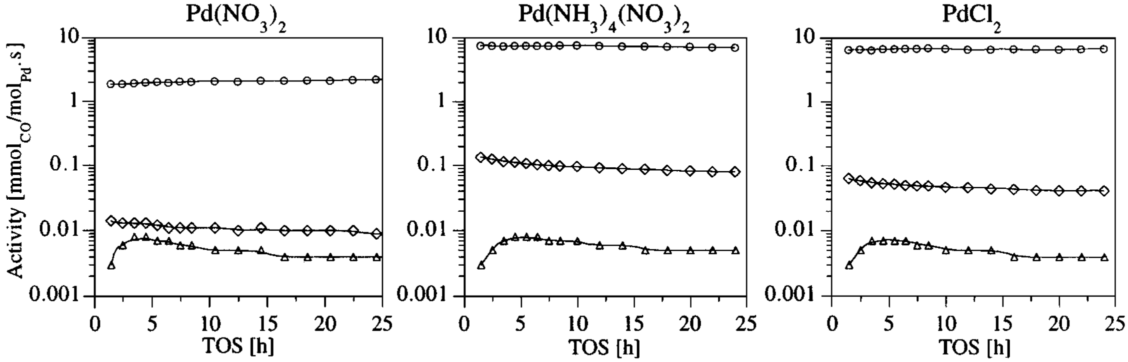


FIG. 2. Product activities in the hydrogenation of CO over Ca/Pd/SiO$_2$ (Ca/Pd = 0.04) prepared from different Pd salts. (◇) CH$_4$, (△) C$_{2+}$, (○) C$_{1\text{-oxo}}$.

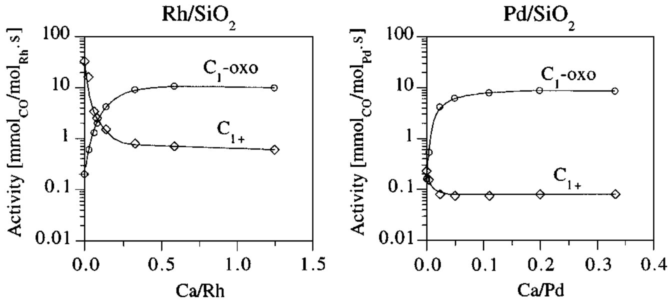


FIG. 3. Effect of adding Ca to Rh/SiO$_2$ and Pd/SiO$_2$ catalysts in the hydrogenation of CO. (◇) C_{1+}, (○) $C_{1\text{-oxo}}$.

catalyst obtained from Pd(NO$_3$)$_2$ had a very low hydrocarbon formation due to the low Pd dispersion and the further suppression of the CO dissociation by the addition of Ca. The higher methanol activity of the Ca/Pd/SiO$_2$ catalysts prepared from PdCl$_2$ and Pd(NH$_3$)$_4$(NO$_3$)$_2$ shows that the Pd particle size influences the methanol formation as well. Catalysts with small Pd particles will have larger CaO–Pd contact areas, resulting in a stronger promotion of the methanol formation. Since, in the preparation of Pd catalysts from the Pd(NH$_3$)$_4$(NO$_3$)$_2$ precursor, high dispersions are obtained and problems due to the formation of HCl during catalyst pretreatment are avoided, all further experiments were carried out with catalysts prepared from this Pd salt.

By testing systems with different Ca/Pd ratios, we observed a clear correlation between the Ca amount and methanol yield (Fig. 3, right hand side). The hydrocarbon formation of undoped Pd/SiO$_2$ is very low because of the modest CO dissociation capacity, and the addition of Ca causes a further decrease of the hydrocarbon formation and a dramatic increase in the methanol formation. Thus, a Ca/Pd ratio larger than 0.05 is sufficient to obtain 99% $C_{1\text{-oxo}}$ selectivity (Table 1). The results in Fig. 3 (left-hand side) show that Rh/SiO$_2$ is about as active in methanol formation as Pd/SiO$_2$ and suppresses hydrocarbon formation relatively even stronger than Pd/SiO$_2$. Nevertheless, since hydrocarbon formation of undoped Rh/SiO$_2$ is 2 orders of magnitude higher than that of undoped Pd/SiO$_2$, it cannot be suppressed strongly enough over Ca/Rh/SiO$_2$ to obtain better than 90% $C_{1\text{-oxo}}$ selectivity.

The addition of Ca also influences the formation of dimethyl ether (Table 1). Acidic sites present on the support, which are responsible for the condensation of surface methoxy groups to dimethyl ether, are neutralized by basic metal oxides (8). Dimethyl ether formation is therefore inhibited by the increasing concentration of basic additives on the catalyst surface.

The slight decrease in activity at high Ca loading is probably due to the decrease in the chemisorption capacity as shown by H$_2$ chemisorption measurements (Table 1). A suppression of the exposed metal surface may be due to coverage of Pd by CaO, or, if the metal oxide additive is distributed as small islands (20), by coalescence of the oxide patches to much larger particles, so that fewer interfacial sites will be present.

CO and CO$_2$ Hydrogenation over X/Pd/SiO$_2$

The $C_{1\text{-oxo}}$ product activities in the hydrogenation of CO over Pd/SiO$_2$ catalysts doped with various metal oxides (X/Pd = 0.125) are presented in Fig. 4. There are substantial variations in the promotional behavior between the different groups of metal oxides (alkali, alkaline earth, rare earth, and transition metals) as well as within the groups themselves (Fig. 4 and Table 2). The La-doped Pd/SiO$_2$ catalyst showed the highest activity in the methanol formation. In addition, the alkaline earth oxides strongly affected the catalytic performance of Pd/SiO$_2$. Large differences in the promotional behavior were observed among the alkali oxides. Thus, only the Li-doped catalyst showed a strong promotion of the methanol synthesis, while, in agreement with previous results (12), the activity decreased in the order Li ≫ Na > K > Rb, Cs. The two catalysts doped with Mn and Zn oxide showed dissimilar properties.

TABLE 1

Catalytic Properties after 24 h of Ca/Pd/SiO$_2$ Catalysts Prepared from Pd(NH$_3$)$_4$(NO$_3$)$_2$

Ca/Pd (molar)	H_{irr}/Pd	Activity (mmol$_{CO}$)/ mol$_{Pd}$ · s	Deact. (% h^{-1})	Selectivities (%)			MeOH/ DME^a
				CH$_4$	C$_{2+}$	$C_{1\text{-oxo}}$	
—	0.26	0.4	0.9	54.7	3.7	41.6	0.7
0.004	0.24	0.7	0.5	21.6	1.1	77.3	0.6
0.02	—	4.3	0.3	1.6	0.1	98.3	18.5
0.05	0.22	7.2	0.4	1.1	0.1	98.8	19.3
0.11	—	8.0	0.0	0.9	0.1	99.0	22.4
0.20	—	8.9	0.0	0.9	0.1	99.0	27.8
0.33	0.18	8.7	0.0	0.9	0.1	99.0	35.6

^{a} Methanol to dimethyl ether ratio.

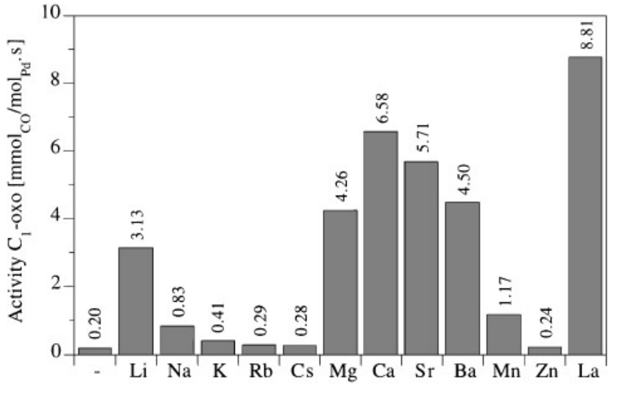


FIG. 4. $C_{1\text{-oxo}}$ activity after 24 h of X/Pd/SiO$_2$ catalysts in the hydrogenation of CO.

TABLE 2

Catalytic Properties after 24 h of X/Pd/SiO_2 (X/Pd = 0.125) in the CO Hydrogenation

Additive	H_{irr}/Pd	Activity ($mmol_{CO}$/$mol_{Pd} \cdot s$)	TOF ($10^{-3} \cdot s^{-1}$)	Selectivities (%)			
				CO_2	CH_4	C_{2+}	$C_{1\text{-oxo}}$
—	0.16	0.3	1.9	12.3	22.1	1.5	64.1
Li	0.17	3.3	19.4	2.8	1.7	0.1	95.4
Na	0.16	0.9	5.6	7.2	1.7	0.6	90.5
K	0.16	0.5	3.1	11.7	3.3	1.4	83.6
Rb	0.16	0.4	2.5	13.7	3.4	0.8	82.1
Cs	0.15	0.4	2.7	14.8	4.2	0.8	80.2
Mg	0.15	4.5	30.0	3.5	1.3	0.1	95.1
Ca	0.16	6.9	43.1	4.2	0.5	0.1	95.2
Sr	0.16	6.0	37.5	4.8	0.4	0.1	94.7
Ba	0.15	4.8	32.0	6.8	0.3	0.1	92.8
Mn	0.16	1.4	8.8	4.2	10.3	1.0	84.6
Zn	0.10	0.3	3.0	14.6	9.1	1.0	75.3
La	0.14	9.6	68.6	5.8	2.4	0.2	91.6
—[a]	0.28	3.6	12.9	12.4	18.0	0.5	69.1
Ca[a,b]		3.3		11.4	12.8	0.5	75.3

[a] Al_2O_3 support.
[b] Ca/Pd = 0.2.

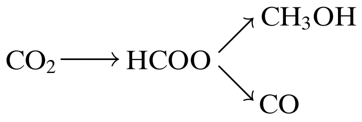
The influence of Mn was moderate, whereas that of Zn was negligible.

Substantial differences were also observed in the performances of X/Pd/SiO_2 catalysts in the synthesis of hydrocarbons (Table 2). The addition of basic oxides was generally accompanied by a suppression of the hydrocarbon formation, which is ascribed to an inhibition of the CO dissociation. Only Mn and La enhanced the hydrocarbon production.

Several authors observed that in the hydrogenation of CO_2, Pd catalysts produce only methane and CO if neutral or acidic supports were used (21, 22). Ramaroson *et al.* (23) reported subsequently that methanol is formed when the reaction is carried out over catalysts supported on basic oxides. Similar to the hydrogenation of CO, it was proposed that both activity and selectivity of the catalyst are affected by the acid–base properties of the metal oxide that is used as an additive or as the support (21, 24, 25).

The catalytic properties of a Pd/SiO_2 catalyst in the hydrogenation of CO_2, as a function of the reaction time, are shown in Fig. 5. The total catalytic activity is about as low as that for CO hydrogenation, but the product distribution is different (cf. Tables 2 and 3). Carbon monoxide, produced by the reverse water–gas shift reaction, was the main product in the conversion of H_2 and CO_2; methane was the only hydrocarbon detected, and methanol was formed only in trace amounts.

The presence of oxidic additives affected not only the formation of methanol but also the conversion of CO_2 in CO (Fig. 6). The total activity of most doped catalysts was more than an order of magnitude higher than that of undoped Pd/SiO_2. However, since the increased catalytic performance is mainly the result of the promotion of the reverse water–gas shift, the methanol selectivity does not show much improvement when metal oxides are added (Table 3). The promotional effect of basic additives on methanol as well as CO formation suggests that methanol synthesis and the reverse water–gas shift reaction have a common reaction intermediate and take place on the same catalytic site. It was proposed (25–27) that both reactions occur through formate species adsorbed on the support:



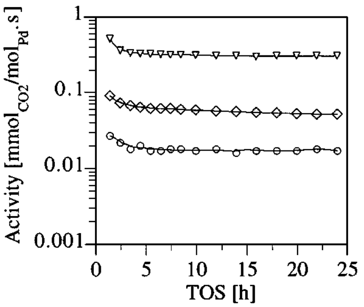


FIG. 5. Product activities of Pd/SiO_2 in the hydrogenation of CO_2. (◇) CH_4, (○) $C_{1\text{-oxo}}$, (▽) CO.

TABLE 3

Catalytic Properties after 24 h of X/Pd/SiO_2 (X/Pd = 0.125) in the CO_2 Hydrogenation

Additive	H_{irr}/Pd	Activity ($mmol_{CO}$/$mol_{Pd} \cdot s$)	TOF ($10^{-3} \cdot s^{-1}$)	Selectivities (%)		
				CO	CH_4	$C_{1\text{-oxo}}$
—	0.16	0.4	2.5	81.8	13.6	4.6
Li	0.17	4.9	28.6	85.2	0.2	14.6
Na	0.16	7.1	44.4	94.8	0.1	5.1
K	0.16	5.0	31.3	95.8	0.1	4.1
Rb	0.16	3.6	22.5	96.7	0.1	3.2
Cs	0.15	2.9	19.3	96.2	0.1	3.7
Mg	0.15	3.5	23.3	81.1	1.2	17.8
Ca	0.16	5.2	32.8	83.3	0.2	16.5
Sr	0.16	6.5	40.6	85.6	0.1	14.3
Ba	0.15	7.9	52.7	87.1	0.1	12.8
Mn	0.16	1.7	10.6	74.9	7.7	17.4
Zn	0.10	0.5	5.0	88.1	3.5	8.4
La	0.14	6.6	47.1	78.7	3.5	17.8
—[a]	0.28	3.6	12.9	49.8	38.4	11.8
Ca[a,b]		3.0		43.2	43.4	13.4

[a] Al_2O_3 support.
[b] Ca/Pd = 0.2.

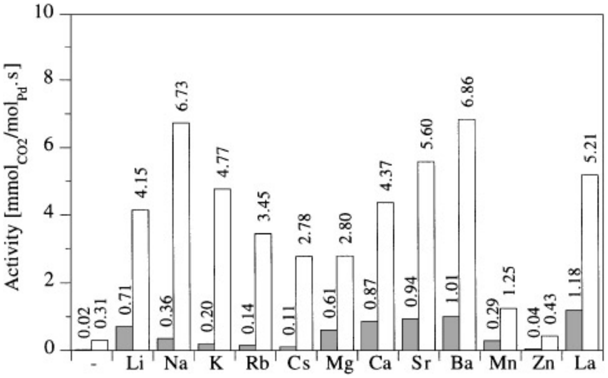


FIG. 6. $C_{1\text{-oxo}}$ and CO activities after 24 h of X/Pd/SiO$_2$ catalysts in the hydrogenation of CO_2. (■) $C_{1\text{-oxo}}$, (□) CO.

where methanol is formed by hydrogenation, and CO by dehydration of this intermediate.

The influence of the reaction temperature on the product activities of Ca/Pd/SiO$_2$ in the hydrogenation of CO and CO_2 is shown in Fig. 7. Reaction temperature had a strong influence on the $C_{1\text{-oxo}}$ activity. Below 560 K, methanol formation is controlled by the reaction rate, while at higher temperatures the yield is limited by thermodynamic equilibrium (28). In the investigated temperature range (503–603 K), the formation of hydrocarbons and the reverse water–gas shift reaction are, however, controlled only by the kinetics. Thus, over the whole temperature range hydrocarbon and CO yields are much lower than the maximal thermodynamic yields.

Arrhenius plots of methanol and methane formation from CO gave apparent activation energies of 58 and 103 kJ/mol, respectively, in good in agreement with the values obtained by Ryndin *et al.* for Pd/Al$_2$O$_3$ and Pd/La$_2$O$_3$ (8). The apparent activation energies for CO_2 hydrogenation to methanol and methane were 48 and 101 kJ/mol, respectively, the latter value being in good agreement with that obtained by Erdöhelyi *et al.* (29).

Hydrogenation of CO/CO$_2$ Mixtures over Ca/Pd/SiO$_2$

As described above, the total rates in the hydrogenation of CO and CO_2 are similar (cf. Tables 2 and 3), but the rate of methanol formation in the hydrogenation of CO_2 is much lower than that in the hydrogenation of CO, since most of the CO_2 is converted to CO while most of the CO goes to methanol. Although CO_2 is known to be the main carbon source of methanol in CO–CO$_2$–H$_2$ mixtures over Cu/ZnO catalysts (30), the rate of methanol formation over Ca/Pd/SiO$_2$ catalysts increased with the CO partial pressure (Fig. 8). The methanol formation was linearly related to the CO partial pressure over a wide range (Fig. 8, dotted line) but was lower than the dotted line in the conversion of the CO-free mixture and higher in the conversion of the CO_2-free mixture. These observations indicate that competitive adsorption of CO and CO_2 on the basic surface sites of the oxidic additive plays a role in the hydrogenation of CO–CO$_2$ mixtures.

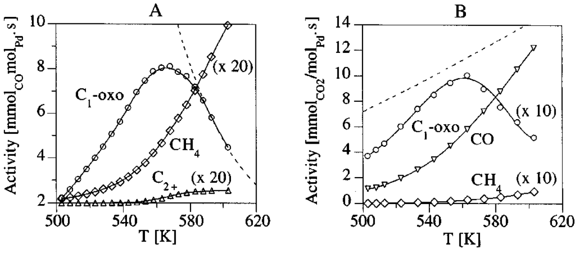


FIG. 7. The effect of the reaction temperature on product activities in the hydrogenation of CO (A) and CO_2 (B) over Ca/Pd/SiO$_2$. (- - -) Thermodynamic yield of methanol (A) and CO (B).

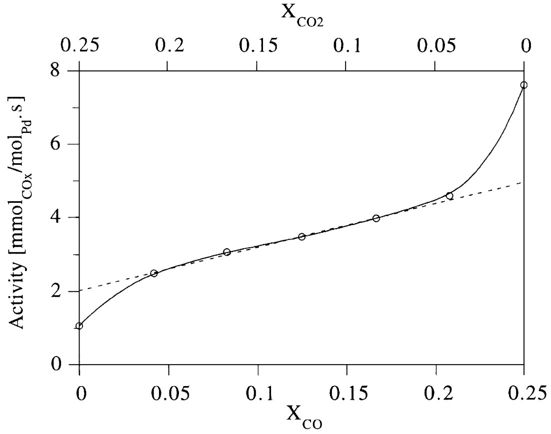


FIG. 8. $C_{1\text{-oxo}}$ activities of Ca/Pd/SiO$_2$ in the conversion of CO/CO$_2$/H$_2$ [x/(0.25$-x$)/0.75] mixtures.

CO and CO$_2$ Hydrogenation over Pd/Al$_2$O$_3$ and Ca/Pd/Al$_2$O$_3$

Supporting the Pd clusters on an amphoteric oxide such as γ-alumina increases the catalyst activity by almost 1 order of magnitude relative to Pd/SiO$_2$ (Table 2). Not only the increased metal dispersion (0.16 for Pd/SiO$_2$ and 0.28 for Pd/Al$_2$O$_3$) but also the chemical characteristics of the support must be taken into consideration to explain this. As reported above for doped Pd/SiO$_2$ catalysts, additives with a basic character positively affect the formation of $C_{1\text{-oxo}}$ products (methanol and dimethyl ether). Apparently, the presence of basic sites on the Al$_2$O$_3$ surface improves the adsorption of CO as formate, while the interaction of the carbonyl oxygen with Lewis acid sites increases the rate of hydrogenation of these intermediates to methanol (25).

The hydrocarbon distribution was also significantly affected by the alumina support. Whereas the methane activity is ten times higher over Pd/Al$_2$O$_3$ than over Pd/SiO$_2$ (Table 2), the production of higher hydrocarbons is only four times higher and still limited to C$_2$–C$_3$ paraffins. It is possible that methane is formed by the hydrogenation of methoxy species adsorbed on the support surface, as suggested by Hsiao and Falconer (31). The increased methane formation could then be a consequence of the higher concentration of methoxy groups and the higher reactivity of these species. On the other hand, the C–C bond formation occurs on the Pd metal surface by insertion of carbene species into an alkyl–metal bond and is affected only indirectly by the support.

In the hydrogenation of CO_2, alumina also improved the catalytic behavior of Pd catalysts substantially, with the Pd/Al_2O_3 catalyst being almost 1 order of magnitude more active than Pd/SiO_2 (Table 3). Alumina positively influences not only the formation of methanol but also the reverse water–gas shift reaction and the production of methane. Methanol synthesis and the reverse water–gas shift reaction may have a common reaction intermediate and take place on the same catalytic site. Formate species, formed by the hydrogenation of carbonate species on the support surface, are hydrogenated to methanol or dehydrated to CO (25–27). The presence of basic sites on the support surface may increase the adsorption of CO_2 in the form of carbonate or hydrogen carbonate species. On the other hand, the acid sites not only activate the hydrogenation of the intermediates but also promote their dehydration to CO (32).

In contrast with Pd/SiO_2, addition of Ca to Pd/Al_2O_2 improved neither the methanol activity in the hydrogenation of CO nor that in the hydrogenation of CO_2 (Tables 2 and 3). In addition, the methanol to dimethyl ether ratio hardly changed (0.3 for CO hydrogenation and 2.5 for CO_2 hydrogenation). These observations suggest that Ca interacts strongly with the acid sites of the alumina support and that the formation of a Pd–CaO interface is much more difficult on a catalyst supported on alumina than it is on a silica-supported catalyst. This may confirm that intimate contact between the palladium metal particle and the oxidic additive is necessary for the enhancement of the methanol formation (12, 20, 24, 33).

DISCUSSION

The results presented in Tables 2 and 3 show that several alkali, alkaline earth, and other metal oxides increase the activity of Pd/SiO_2 catalysts for the formation of methanol from H_2 and CO as well as from H_2 and CO_2 by an order of magnitude or more. It is clear that, in contradiction to former claims (2), Pd alone is not a good methanol catalyst. The ability to adsorb CO molecularly and H_2 dissociatively is not sufficient to form methanol, and the small amount of methanol produced by the Pd on an ultrapure SiO_2 catalyst may even be caused by low levels of impurities.

The small and sometimes negligible variations in the chemisorption capacities of most of the $X/Pd/SiO_2$ catalysts (Table 2) demonstrate that differences in the Pd surface area or particle size are not responsible for the variations of the methanol activities. Only the Zn-doped catalyst had a noticeably lower H_{irr}/Pd ratio. It is conceivable that ZnO reacts with hydrogen atoms, formed on the Pd surface and spilled over onto the support, to Zn hydride or even to metallic Zn which may migrate to the Pd surface (34). The formation of a Pd–Zn alloy would explain the decrease in the hydrogen chemisorption.

Catalysts made from noble metal chlorides are often more active than those made from other salts, and this has sometimes been explained by an influence of chlorine on the catalysis (8, 12–14). In our catalysts, the Cl^- and NO_3^- anions had completely disappeared after calcination and reduction, so that the anion could only have an indirect effect on the catalyst activity. The catalysts made from $Pd(NH_3)_4(NO_3)_2$ and $PdCl_2$ on ultrapure SiO_2 had, however, similar Pd dispersions and similar activities and selectivities. It might very well be that differences between catalysts, as described in the literature (2, 7, 14, 35), are due to the use of impure supports. Metal salt solutions, especially those from metal chlorides, can be aggressive and leach alkali and alkaline earth ions out of the glassware used in catalyst preparation. For that reason we prepared our supports and the catalysts in well-rinsed polyethylene beakers (see Experimental). Leaching by the metal salt solution during catalyst preparation may also explain the differences observed between catalysts prepared on different commercial SiO_2 supports. Even the seemingly low Ca impurity levels of Davison grades 01 and 57 (0.006 and 0.06 wt%, respectively) mean that the 5 wt% Pd/SiO_2 catalysts of Kelly *et al.*, made from these supports, contained Ca/Pd ratios of 0.003 and 0.03, respectively (14). If the calcium had been leached out of the support and deposited next to the noble metal particles, the results in Table 1 demonstrate that this could have led to increases in activity by factors of about 2 and 12, respectively, compared to a calcium-free catalyst. The observed suppression of methanol activity upon the addition of basic metal cations (35) might also be due to impurities in the support. Exchange of active impurity cations (e.g. calcium) by less active cations (K, Rb, Cs) during impregnation of a Pd/SiO_2 catalyst, made from a calcium-containing SiO_2, would lead to a decrease in activity.

The promotion of methanol formation by basic metal oxides is not restricted to Pd. This was observed previously for other metals such as Rh and Cu; as far as Rh is concerned, little attention had been paid to it, with the exception of mechanistic aspects (3, 4). The main reason was that Rh is a much more active catalyst for CO dissociation and, therefore, even though Ca promotes methanol formation of a Rh/SiO_2 catalyst about as well as it does of a Pd/SiO_2 catalyst, it does not suppress hydrocarbon promotion to such an extent (Fig. 3). As a consequence, a $Ca/Rh/SiO_2$ catalyst can be as productive a methanol catalyst as $Ca/Pd/SiO_2$ though less selective (90 rather than 99%).

For Rh catalysts, the prevalent opinion is that the promoter is located on or close to the metal particles, probably as metal oxide patches (4). Catalysis may then take place at the interface between noble metal and metal oxide promoters (36). Ponec proposed that the metal oxide stabilizes Rh cations which may insert CO into a Rh^+–H bond. The resulting formyl species is subsequently hydrogenated on metallic Rh to methanol (4). Others have suggested that a CO molecule on the surface of the noble metal may react with chemisorbed O and H atoms to formate (34, 37), just as CO_2 reacts with metal hydride complexes to formate complexes (38–40). Methanol is then formed by hydrogenation of formate, again at the metal surface. The role of basic promoters would then be to stabilize the formate species at the noble metal surface (38).

A third model is based on bifunctionality of the noble metal plus the basic metal oxide catalyst (41). As in the industrial process for formic acid, in which CO and methanol react to methyl formate over a basic catalyst (39, 40, 42), CO may react with a hydroxyl group at the surface of a basic metal oxide patch to formate (43). This formate can then be hydrogenated either by hydrogen atoms, which spill over from the metal particles to the basic metal oxide surface (12, 20, 23, 41, 44), or by hydrogen atoms on the noble metal after migration of the formate species to the metal surface (26). Alternatively, the formate could react with methanol to methyl formate on the basic metal oxide, followed by diffusion of methyl formate through the gas phase to the surface of a noble metal particle and hydrogenolysis to two methanol molecules (33). In this case, the catalytic cycle must be started by the promotion of a first methanol molecule via one of the other routes.

The increase in methanol formation of $Ca/Pd/SiO_2$ in the hydrogenation of $CO-CO_2$ mixtures with increasing CO content and the decrease in methanol formation when going from Li to Cs as a promoter in $X/Pd/SiO_2$ catalysts is quite different to the behavior of promoted Cu catalysts (26, 45, 46). It suggests that, in contrast to Cu/ZnO, where CO_2 is the carbon source of methanol (30), CO is the source of methanol over $Ca/Pd/SiO_2$. This supports the idea that formate is the crucial intermediate for $Ca/Pd/SiO_2$, because it can be easily formed by the reaction of CO with a basic OH group on the surface of the metal oxide. The presence of formate on the catalyst support surface during the synthesis gas reaction (12, 29) or when exposed to CO (43) is well documented for amphoteric and basic supports. On silica, however, formate is detected only when the silica is doped with alkali metal cations (43, 44). Notwithstanding this excellent correlation between methanol activity and the presence of formate on the support surface, formate has usually been regarded as a spectator species and not as a reaction intermediate.

The promoting effect of the alkali and alkaline earth metal oxides on the silica-supported Pd catalysts suggests that basic oxide additives, close to or on the Pd particles, are directly involved in the methanol synthesis. The fact that Ca has hardly any effect on alumina-supported Pd catalysts indicates that the promoter should also be close to or in contact with the metal particle. The distribution of the additives over the silica and Pd surface in the Pd/SiO_2 catalysts and their presence in the form of (basic) metal oxide patches or (nonbasic) metal silicates are not known yet. Studies of Rh/SiO_2 catalysts promoted with La and Pd/SiO_2 catalysts promoted with Na have shown that the promoter and noble metal particles are in close contact (47, 48). Further studies to answer these questions are in progress.

The substantial differences in the effect of the metal oxides show that the presence of basic metal oxide patches close to the Pd surface is not the only factor which determines methanol synthesis. Intrinsic characteristics of the metal oxide, such as acid–base properties and density of surface sites, affect the performance of the catalyst as well (8, 12, 41). The acid–base properties of a metal oxide are related to the electronegativity of its metal cation (49–51). Tanaka and Ozaki proposed (52) that the electronegativity of cations in oxidic materials (EN_i) is related to the Pauling electronegativity EN_0 of the element and the oxidation state Z of the cation: $EN_i = EN_0\,(1 + 2Z)$.

Figure 9 shows the degree of rate enhancement of the doped catalysts relative to the undoped Pd/SiO_2 catalyst for the methanol formation as a function of the electronegativity EN_i of the additive cation. Additives with low cation electronegativity (strong basic character) as well as oxides with high cation electronegativity (Lewis acid) have hardly any effect on the rate of methanol formation or are only modest promoters, while metal oxides with a moderate basic nature, such as the oxides of the alkaline earth metals, or with amphoteric properties, such as La_2O_3, strongly increase the methanol formation. Thus a clear

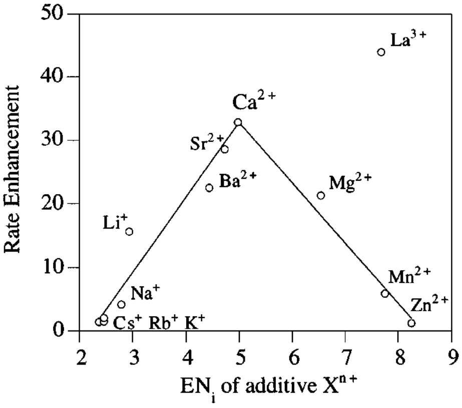


FIG. 9. Rate enhancement for $C_{1\text{-oxo}}$ formation in the hydrogenation of CO as a function of the electronegativity (EN_i) of the additive cation.

volcano-shaped correlation is established between cation electronegativity and methanol formation. This supports the idea that the basic (nucleophilic) OH groups present on the oxide surface are responsible for the formation of formate species and that the hydrogenation rate of these intermediates is also related to the acid–base properties of the additive (25, 53). Metal oxides with low EN_i enhance the surface concentration of formate, but their strong basic nature causes an excessive stabilization of this intermediate. As a consequence, the hydrogenation of formate to methanol is reduced by the weaker electrophilic character of the carbonyl carbon. On the other hand, metal oxides with Lewis acid properties may increase the rate of formate hydrogenation but, at the same time, the formation of adsorbed formate is diminished by the weak nucleophilic character of the surface OH groups. For these reasons, it is not surprising that La_2O_3 dramatically increases the methanol formation and that it is situated above the volcano curve. As an amphoteric oxide, La_2O_3 can adsorb CO as a formate species on the basic sites and can activate the formate for the hydrogenation to methanol by the acid sites.

The differences in the performance of the $X/Pd/SiO_2$ catalysts in the hydrogenation of CO_2 can be related to the acid–base properties of the metal oxides as well. A clear volcano-shaped correlation exists between cation electronegativity (as a measure of the acid–base properties) and the methanol formation (Fig. 10), and the rate enhancements induced by the different additives are of similar magnitude as those obtained in the CO hydrogenation. This supports the idea that the formation of methanol from CO as well as CO_2 occurs through the same reaction intermediate (formate), and that the active sites involved in the catalytic reactions are also the same. The presence of a basic oxide on the support may enhance the adsorption of CO_2 in the form of surface carbonate (54). This species is subsequently hydrogenated to formate by hydrogen activated on the Pd surface and spilled over onto the support from which methanol or CO can be formed.

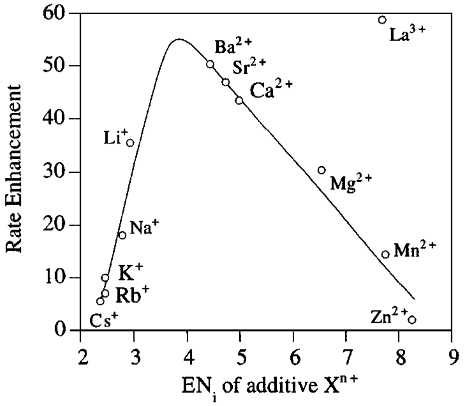


FIG. 10. Rate enhancement for $C_{1\text{-oxo}}$ formation in the hydrogenation of CO_2 as a function of the electronegativity (EN_i) of the additive cation.

While all added metal oxides increased the formation of methanol, most of them decreased the formation of hydrocarbons (Table 2). This might be ascribed to a coverage of the Pd kink and corner sites where CO dissociation is supposed to occur (18, 19). Only the acid MnO and amphoteric La_2O_3 oxides increased the formation of hydrocarbons (Table 2). This has also been observed for Rh catalysts and explained by an interaction between the oxygen atom of adsorbed CO or H_nCO and acid sites of the metal oxide. This promotes the CO dissociation process and, thus, the formation of surface CH_x species which lead to hydrocarbons (50).

CONCLUSIONS

Contrary to claims made in the past for supported Pd catalysts but in agreement with studies of unsupported Pd catalysts, the results obtained with the Pd catalyst supported on impurity-free SiO_2 demonstrate that Pd is not a good methanol catalyst. Molecular adsorption of CO and the availability of activated hydrogen are not sufficient for the formation of methanol. Basic metal oxides are needed to give a Pd catalyst a high activity for methanol formation from CO and H_2. The clear correlation between Ca loading and methanol formation supports the assumption that the reaction takes place on *bifunctional* catalysts. Sites on the metal oxide are responsible for the formation of the formate species, and Pd activates hydrogen for the further hydrogenation steps.

The hydrogenation of CO and CO_2 over $X/Pd/SiO_2$ catalysts showed that the promoting effect of the additives on the methanol formation is related to their acid–base properties. Basic sites increase the concentration of adsorbed formate, whereas sites with Lewis acid properties can activate this intermediate for the hydrogenation to methanol. This further supports the suggestion that formate species are intermediates and that the additives are directly involved in the catalytic formation of methanol, i.e. that basic metal oxides are not merely promoters but act as *co-catalysts*.

While CO_2 is the main carbon source of methanol over Cu/ZnO catalysts, CO is the main source over a $Ca/Pd/SiO_2$ catalyst. High CO partial pressures may inhibit the reverse water–gas shift reaction, the decomposition of the formate species in water and CO and thus favor the hydrogenation of formate to methanol.

The use of Al_2O_3 as a support strongly improved the Pd catalyst activity. This can be ascribed not only to an increased metal dispersion but also to the amphoteric properties of the support. The lack of a promotional effect of Ca in alumina-supported catalysts indicates that the strong interaction of this basic additive with the acid sites of the support suppresses the mobility of Ca on the surface and prevents the formation of the catalytically active CaO–Pd interface.

Our results show that, for certain catalytic reactions, it is not enough to use a commercial support of high purity but that extreme precautions must be taken to avoid impurities. It is common knowledge in surface science that single crystal surfaces should be carefully treated before use, because impurities, even at the ppm level, often end up at the surface and modify the catalysis; for supports this is less well known. For a support such as alumina which has reasonably strong acidic as well as basic surface sites, impurities in the support or introduced during wet catalyst preparation constitute much less of a problem. In such a support the impurities are quite strongly bonded, and because the support has a much larger surface area than the active catalyst, the chance of an impurity being located next to a catalyst particle is negligible. On a support like silica, on the other hand, the impurities are weakly bonded and can move during catalyst preparation and end up next to the active catalyst particles. In that position they can have a strong influence on the catalysis. The impurity level of silica must be in the ppm level or below in order to observe the intrinsic catalytic properties of the catalyst particles themselves.

REFERENCES

1. German Patent 293 787, 1913.
2. Poutsma, M. L., Elek, L. F., Ibarbia, P. A., Risch, A. P., and Rabo, J. A., *J. Catal.* **52**, 157 (1978).
3. Sachtler, W. M. H., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. I, p. 151. Dechema, Frankfurt-am-Main, 1984.
4. Ponec, V., *Stud. Surf. Sci. Catal.* **64**, 117 (1991).
5. Rabo, J. A., Risch, A. P., and Poutsma, M. L., *J. Catal.* **53**, 295 (1978).
6. Vannice, M. A., *J. Catal.* **37**, 449 and 462 (1975).
7. Fajula, F., Anthony, R. G., and Lunsford, J. H., *J. Catal.* **73**, 237 (1982).
8. Ryndin, Y. A., Hicks, R. F., Bell, A. T., and Yermakov, Y. I., *J. Catal.* **70**, 287 (1981).
9. Nonneman, L. E. Y., Bastein, A. G. T. M., Ponec, V., and Burch, R., *Appl. Catal.* **62**, L23 (1990).
10. Nonneman, L. E. Y., and Ponec, V., *Catal. Lett.* **7**, 213 (1990).
11. Kaiser, S. W., EP 0031 243 and 0031 244, 1981, Union Carbide.
12. Kikuzono, Y., Kagami, S., Naito, S., Onishi, T., and Tamaru, K., *Faraday Discuss. Chem. Soc.* **72**, 135 (1981).
13. Driessen, J. M., Poels, E. K., Hindermann, J. P., and Ponec, V., *J. Catal.* **82**, 26 (1983).
14. Kelly, K. P., Tatsumi, T., Uematsu, T., Driscoll, D. J., and Lunsford, J. H., *J. Catal.* **101**, 396 (1986).
15. Gloor, A. P., and Prins, R., *Rec. Trav. Chim. Pays-Bas* **113**, 481 (1994).
16. Gotti, A., and Prins, R., *Catal. Lett.* **37**, 143 (1996).
17. Vis, J. C., van 't Blik, H. F. J., Huizinga, T., van Grondelle, J., and Prins, R., *J. Mol. Catal.* **25**, 367 (1984).
18. Ichikawa, S., Poppa, H., and Boudart, M., *J. Catal.* **91**, 1 (1985).
19. Matolin, V., Rebholz, M., and Kruse, N., *J. Catal.* **105**, 366 (1987).
20. Bailie, J. E., Rochester, C. H., and Millar, G. J., *Catal. Lett.* **31**, 333 (1995).
21. Vannice, M. A., *J. Catal.* **40**, 129 (1975).
22. Solymosi, F., Erdöhelyi, A., and Kocsis, M., *J. Catal.* **65**, 428 (1980).
23. Ramaroson, E., Kieffer, R., and Kiennemann, A., *J. Chem. Soc. Chem. Commun.* **12**, 645 (1982).
24. Fujita, S., Usui, M., Hanada, T., and Takezawa, N., *React. Kinet. Catal. Lett.* **56**, 15 (1995).
25. Tagawa, T., Nomura, N., Shimakage, M., and Goto, S., *Res. Chem. Intermed.* **21**, 193 (1995).
26. Clarke, D. B., and Bell, A. T., *J. Catal.* **154**, 314 (1995).
27. Fischer, I. A., Woo, H. C., and Bell, A. T., *Catal. Lett.* **44**, 11 (1997).
28. Chang, T., Rousseau, R. W., and Kilpatrick, P. K., *Ind. Eng. Chem. Process Des. Dev.* **25**, 477 (1986).
29. Erdöhelyi, A., Pásztor, M., and Solymosi, F., *J. Catal.* **98**, 166 (1986).
30. Chinchen, G. C., Denny, P. J., Parker, D. G., Spencer, M. S., and Whan, D. A., *Appl. Catal.* **30**, 333 (1987).
31. Hsiao, E. C., and Falconer, J. L., *J. Catal.* **132**, 145 (1991).
32. Rhodes, C., Hutchings, G. J., and Ward, A. M., *Catal. Today* **23**, 43 (1995).
33. Fakley, M. E., Jennings, J. R., and Spencer, M. S., *J. Catal.* **118**, 483 (1989).
34. Waugh, K.C., *Catal. Today* **15**, 51 (1992).
35. Kazi, A. M., Chen, B., Goodwin, J. G., Jr., Marcelin, G., Rodriguez, N., and Baker, R. T. K., *J. Catal.* **157**, 1 (1995).
36. Levin, M. E., Salmeron, M., Bell, A. T., and Somorjai, G. A., *J. Catal.* **106**, 401 (1987).
37. Klier, K., *Stud. Surf. Sci. Catal.* **19**, 439 (1984).
38. Darensbourg, D. J., and Ovalles, C., *Chem. Technol.* 636 (1985).
39. Jessop, P. G., Ikariya, T., and Noyori, R., *Chem. Rev.* **95**, 259 (1995).
40. Leitner, W., *Angew. Chem., Int. Ed. Engl.* **34**, 2207 (1995).
41. Mériaudeau, P., Dufaux, M., and Naccache, C., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 2, p. 185. Dechema, Frankfurt-am-Main, 1984.
42. Andreoni, M., Raspolli Galletti, A. M., and Sbrana, G., *Catal. Lett.* **38**, 127 (1996).
43. Gopal, P. G., Schneider, R. L., and Watters, K. L., *J. Catal.* **105**, 366 (1987).
44. Naito, S., Yoshioka, H., Orita, H., and Tamaru, K., *in* "Proceedings, 8th International Congress on Catalysis," Berlin, Vol. 3, p. 207. Dechema, Frankfurt-am-Main, 1984.
45. Sheffer, G. R., and King, T. S., *J. Catal.* **116**, 488 (1989).
46. Gotti, A., and Prins, R., *J. Catal.* [To be published]
47. Borer, A. L., and Prins, R., *J. Catal.* **144**, 439 (1993).
48. Liotta, L. F., Martin, G. A., and Deganello, G., *J. Catal.* **164**, 334 (1996).
49. Tanabe, K., *in* "Catalysis Science and Technology," Vol. 2, p. 231. Springer-Verlag, Berlin, 1981.
50. Boffa, A., Lin, C., Bell, A. T., and Somorjai, G. A., *J. Catal.* **149**, 149 (1994).
51. Kässner, P., and Baerns, M., *Appl. Catal. A* **139**, 107 (1996).
52. Tanaka, K.-I., and Ozaki, A., *J. Catal.* **8**, 1 (1967).
53. Lavalley, J. C., *Catal. Today* **27**, 377 (1996).
54. Solymosi, F., Erdöhelyi, A., and Lancz, M., *J. Catal.* **95**, 567 (1985).