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Effect of metal oxide additives on the CO hydrogenation to methanol over Rh/ SiO_2 and Pd/ SiO_2

A. Gotti and R. Prins

Laboratory for Technical Chemistry, Swiss Federal Institute of Technology, 8092 Zurich, Switzerland

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Catalysts were prepared from ultra pure SiO_2, Pd and Rh nitrates and chlorides, and by doping with Al, Fe, Na, K or Ca nitrate. The activities and selectivities of the Pd and Rh catalysts were investigated at 553 K, $H_2/CO = 2$ or 3 and 2.5 or 4 MPa respectively. Additives had a strong influence on the catalytic properties. The doping with alkali and alkaline earth oxides led to a strong suppression of the CO dissociation. Particularly basic additives, such as Ca, had a strong promoting effect on the methanol production. This may confirm that the formation of methanol occurs through formate intermediates.

Keywords: methanol synthesis; Rh catalysts; Pd catalysts; impurity-free SiO_2 support; metal oxide additives; formate intermediate

1. Introduction

Interest in CO hydrogenation is due not only to its industrial applications, but also to its academic challenges. A wide variety of products such as methane, higher hydrocarbons, methanol, ethanol and other oxygenated compounds can be formed, and the wide product distribution is affected by the choice of the active metal, catalyst support, promoters, catalyst pretreatment and reaction conditions.

Even after more than a decade of intensive surface science studies, the elementary steps in the catalyzed conversion of synthesis gas are not completely clear. Whereas the model in which, after dissociative adsorption of H_2 and CO, the formed surface CH_x fragments build hydrocarbons as well as higher oxygenated compounds through CO insertion is well accepted [1–5], the mechanism of the methanol formation and the nature of the catalytic sites are still under debate as shown in two articles, which come to different conclusions in one and the same journal [6,7].

Oxo formation is improved when, in addition to a Group VIII metal, another element is present which can promote CO insertion into metal–alkyl bonds and stabilize the oxo intermediates (acyl, formate, formyl). The prevalent opinion is that the promoter is located on or close to the noble metal surface, probably as oxide patches [8]. Catalysis may then take place at the metal (Group VIII)–metal oxide interface [9]. It has been demonstrated that basic oxides promote the hydrogenation of CO to methanol. Some authors proposed that such additives may stabilize noble metal cations, which may insert CO into a metal cation hydride bond, and that the resulting formyl species is hydrogenated on the metal surface to methanol (fig. 1A) [7,10]. On the other hand, Klier [11] and, more recently, Waugh [12,13] have suggested that metal atoms in contact with surface oxygen anions are sufficiently basic to transform CO or CO_2 into formate (fig. 1B). This species is then hydrogenated to methanol at the metal surface. Basic promoters might play a role in keeping the oxygen anions at the metal surface. Others suggested that the formation of methanol takes place on the support, rather than on the metal (fig. 1C). CO is thought to react on the basic oxide to formate which can be subsequently hydrogenated either by "spilled-over" hydrogen atoms diffusing from the metal particles to the metal oxide surface [4,14–17] or on the noble metal surface after migration from the basic oxide [18]. Another point of interest is the role of support impurities on the catalyst activity. As shown by Nonneman et al. [19,20], catalysts made from very pure SiO_2 had totally different properties to catalysts made from commercial SiO_2. Contaminants in or on the support, which can be easily transferred onto the metal surface during the catalyst preparation, were considered to be responsible for these differences.

By analyzing the catalytic properties of Rh/ SiO_2 and Pd/ SiO_2 catalysts prepared from chloride and nitrate salts, we were able to study the effect of residual anions on the noble metal surface. The intentional doping of ultra pure SiO_2 with alkali, alkaline earth and trivalent Fe and Al cations has enabled us to estimate the influence of support impurities on the catalytic properties. Ca-doped Rh and Pd catalysts were also employed to investigate the role of basic metal oxides in the CO hydrogenation to methanol.

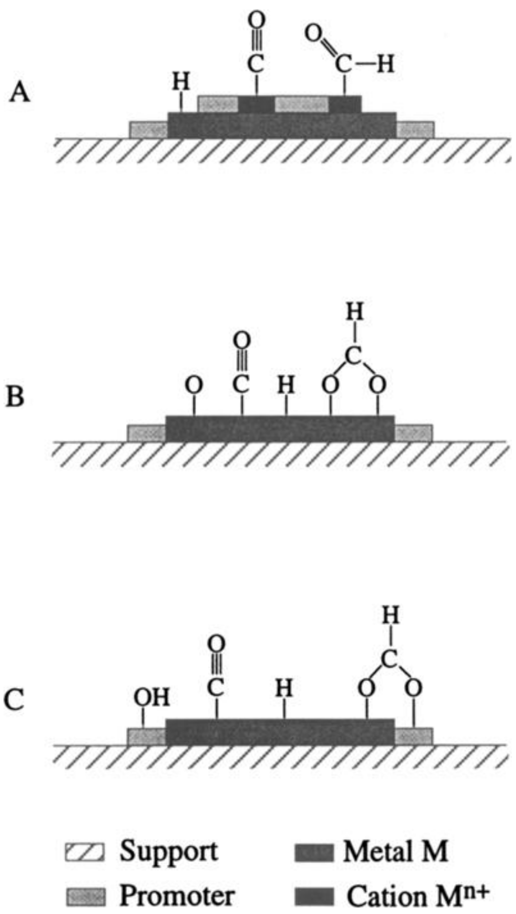

Fig. 1. Possible reaction pathways for methanol formation and schematic description of the catalytic sites [21].

2. Experimental

2.1. Catalyst preparation

Ultra pure SiO_2 was prepared by hydrolysis of tetraethoxysilane [22]. The resulting silica had a BET surface area of 890 m^2/g and an average pore diameter of 5 nm. Doped supports were made by pore-volume impregnation of the ultra pure SiO_2 with aqueous solutions of aluminium, iron, calcium, sodium and potassium nitrate. After impregnation, the supports were dried at 393 K for 16 h and calcined in air at 723 K for 2 h. During calcination, the metal nitrates were transformed into metal oxides and perhaps even into metal silicates by reaction with the silica support.

M/SiO_2 and $M/X/SiO_2$ catalysts ($M = Rh, Pd$; $X = Na, K, Ca, Fe, Al$) were made by pore-volume impregnation of ultra pure and impurity-doped SiO_2 with aqueous solutions of various Pd and Rh salts. The resulting catalyst precursors were dried at 393 K for 16 h. $X/M/SiO_2$ catalysts were prepared by a reverse impregnation sequence. Ultra pure SiO_2 was impregnated with an aqueous solution of the noble metal salt, dried at 393 K for 16 h and calcined in air at 723 K for 2 h. The $X/M/SiO_2$ catalysts were obtained by impregnating the M/SiO_2 precursors with nitrate solutions of the doping elements followed by drying at 393 K for 16 h and calcination at 723 K for 2 h. The metal loading was 1.5% (w/w) for the Rh catalysts and 4.5% (w/w) for the Pd catalysts.

2.2. Catalytic measurements

CO hydrogenation was performed in a steel apparatus equipped with an internal quartz reactor to avoid unintentional contamination of the catalyst with Fe, Ni or Cr formed from metal carbonyls by 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 [23]. The catalyst precursors were reduced in a flow of pure H_2 at 723 K and 0.1 MPa for 1 h. After cooling to 553 K, the hydrogen pressure was increased to working pressure, and CO was added stepwise to the gas flow. Unless stated otherwise, the Pd catalysts were tested at 553 K, 2.5 MPa, $H_2/CO = 2$ and at a space velocity of 770 h^{-1}, the Rh catalysts at 553 K, 4 MPa, $H_2/CO = 3$, and at a space velocity of 10000 h^{-1}. All reactions were carried out under differential conditions. In order to better control the reaction conditions, the gas flows were regulated by mass flow controllers, the pressure was stabilized by means of an electronic upstream pressure controller, and the temperatures of both the oven and the catalyst bed were measured by thermocouples and adjusted by means of proportional-integral-derivative temperature controllers. Reaction products were measured by a computer-interfaced on-line GC.

Hydrogen chemisorption was performed on catalysts reduced in pure H_2 at 723 K for 1 h and evacuated at 10^{-2} Pa for 1 h. Measurements were done at 293 K in the 10–40 kPa range, and the data were extrapolated to 0 kPa. While the total H/Rh values were determined for the Rh catalysts, a correction for bulk hydride formation had to be applied for the Pd catalysts. Thus, after the first hydrogen chemisorption, the Pd catalyst was reevacuated at 10^{-2} Pa for 20 min, and the measurement was repeated. The corrected H_{irr}/Pd value was then obtained as $H_{tot}/Pd - H_{rev}/Pd$.

3. Results and discussion

3.1. CO hydrogenation over Rh/SiO_2

The CO hydrogenation activities and selectivities on Rh/SiO_2 catalysts made from rhodium nitrate and chloride are presented in fig. 2. Both catalysts produced mainly methane, higher hydrocarbons, acetaldehyde but no ethanol, and only trace amounts of methanol, as observed before [19,23]. These results are independent of the precursor salt, that is of the residual anion. This is in contradiction to results published before. According

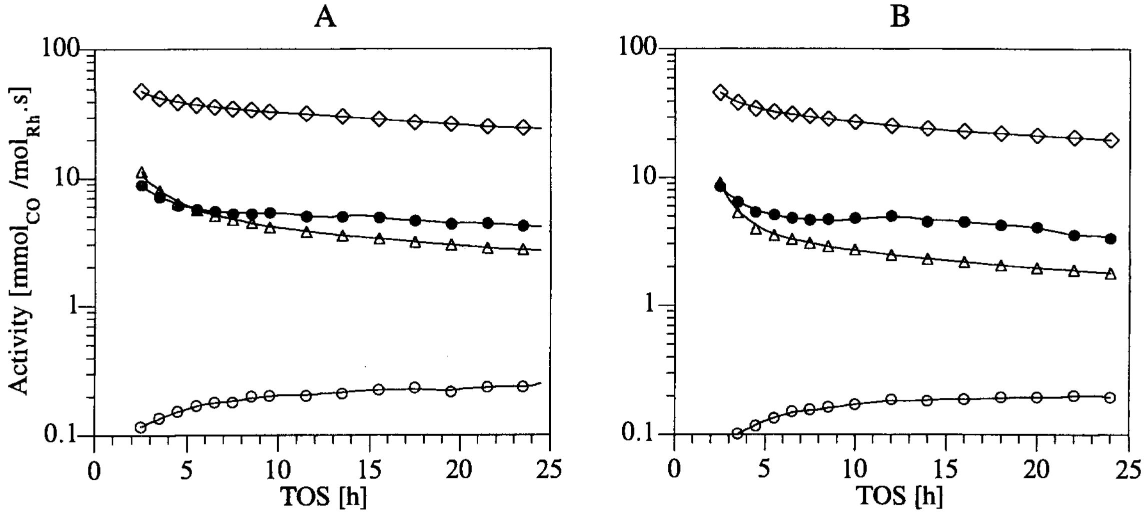

Fig. 2. Product activities in the CO hydrogenation over Rh/SiO$_2$ prepared from (A) Rh(NO$_3$)$_3$ or (B) RhCl$_3$. (◇) CH$_4$, (△) C$_{2+}$, (○) C$_{1oxo}$, (●) C$_{2oxo}$.

to some authors [22,24–26] chloride-containing precursors lead to high activity catalysts, whereas others [27] claimed nitrate precursors to be better. Common to all these investigations is the higher hydrocarbon selectivity for the more active catalysts, independent of the precursor salt, with or without chloride. This correlation between selectivity and activity suggests that variations in the reaction temperature due to heat production, not the possible presence of chlorine in the active catalyst [22] or the different particle morphology [24,25], affected the catalytic properties.

CO hydrogenation activity tests on Rh/SiO$_2$ catalysts, performed at different space velocities, showed that reactions carried out with high catalyst loading were distinguished by an increase in the temperature of the bed and by the absence of oxygen-containing products (fig. 3A). At higher space velocity (fig. 3B), the reaction profile was, however, totally different. Initially there was a significant increase in the temperature of the bed, a high hydrocarbon activity, and an absence of oxo-products. This initial period was followed by a gradual increase in the oxygenate activity, a decrease in the hydrocarbon activity, and a simultaneous cooling down of the catalyst. Finally, reaction stability was established, and the catalytic behaviour was characterized by the usual product distribution (methane $\gg$ oxo-products $>$ higher hydrocarbons). For reactions carried out at high space velocity (10000 h^{-1}), steady state conditions were reached very soon, and no substantial variations in the catalyst temperature or in the product distribution were observed (fig. 2).

As previously observed by Krishnamurty et al. [28], an increase in reaction temperature led to a significant decrease in oxygenate activity (fig. 4). Thermodynamic

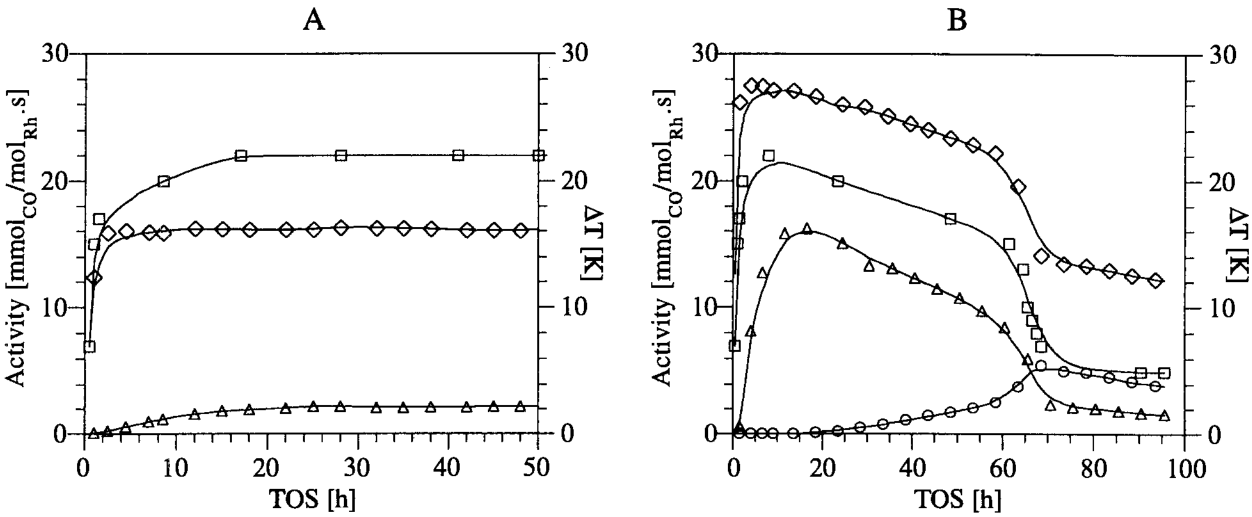

Fig. 3. Product activities in the CO hydrogenation over Rh/SiO$_2$ prepared from RhCl$_3$. (A) SV = 1700 h^{-1}, (B) SV = 2500 h^{-1}. (◇) CH$_4$, (△) C$_{2+}$, (○) oxo$_{tot}$, (□) $\Delta T = T_{bed} - T_{oven}$.

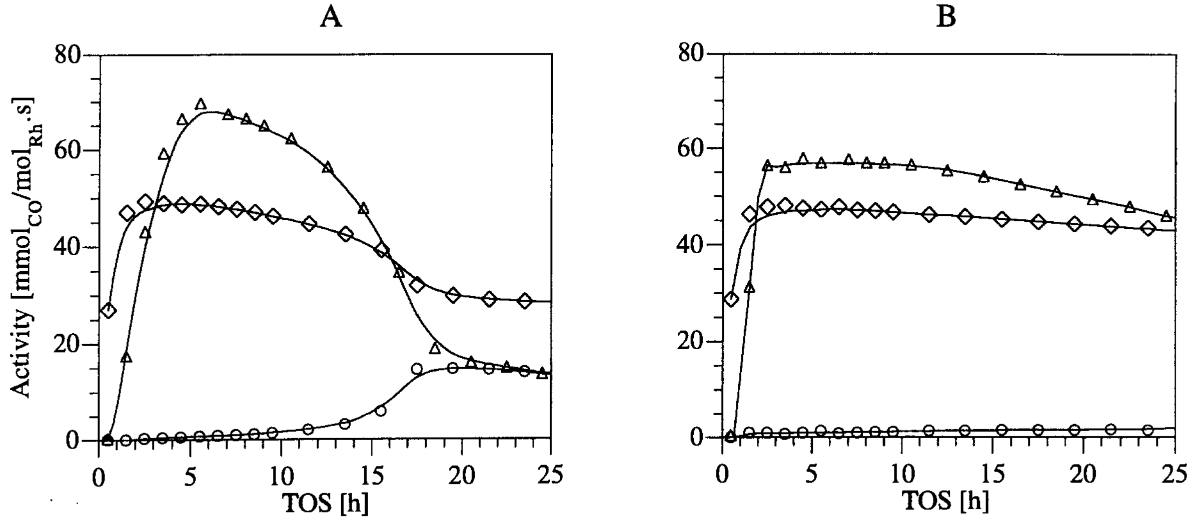

Fig. 4. The effect of reaction temperature in the CO hydrogenation over Rh/SiO$_2$ prepared from Rh(NO$_3$)$_3$ SV = 4600 h^{-1}. (A) T_{bed} = 553 K, (B) T_{bed} = 573 K. (◇) CH$_4$, (△) C$_{2+}$, (○) oxo$_{tot}$.

and kinetic arguments were used to explain this effect: at higher temperature, formation of oxygenates becomes less favoured and hydrogenation to CH$_x$ competes with CO insertion leading to an increase in hydrocarbon selectivity. The above results show that the reaction temperature has a dramatic influence on activity and selectivity, and that unstable operating conditions can easily be obtained under non-differential conditions.

3.2. *CO hydrogenation over impurity-doped Rh/SiO$_2$*

In accordance with Nonneman et al. [19], large differences were observed between the catalytic properties of the catalyst supported on pure SiO$_2$ and the Rh/X/SiO$_2$ catalysts doped with 1000 ppm (molar) Na, K, Ca, Al or Fe. The undoped, the Al- and the Fe-doped catalysts showed similar total activities, while the alkali and alkaline earth doping of the supports resulted in an important inhibitory effect, probably due to the suppression of CO dissociation (table 1) [29,30].

Catalysts with impurity-modified supports had completely different product distribution too (table 1). The alkali and alkaline earth-doped catalysts promoted the CO hydrogenation to methanol; this effect was attributed to the capacity of such modified catalysts to build formate species at the metal–promoter interface [4,31–34] and subsequently to hydrogenate them to methanol (fig. 1). The catalysts doped with amphoteric oxides, such as Al, showed a lower oxygenate product activity and an increase in the formation of higher hydrocarbons, probably as a consequence of the acid catalyzed hydrogenolysis of the oxygen-containing compounds [35]. As previously reported [19,23,36,37], doping of support with Fe resulted in a strongly enhanced production of ethanol at the cost of acetaldehyde. Thus, when promoted by reducible oxides, rhodium tends to produce ethanol because of the enhanced availability of hydrogen and the increased stability of the surface acetyl intermediates.

Because of the great interest in and the controversy about the mechanism and the catalysis of methanol formation, we focused our investigations on the properties of Ca-doped Rh catalysts. To be sure that only the increasing amounts of the doping element were responsible for the variations in the catalytic properties and that resolubilization of the dopant played no role, Ca/Rh/

Table 1
Catalytic properties after 24 h of Rh/SiO$_2$ catalysts prepared from Rh(NO$_3$)$_3$ and doped with 1000 ppm (molar) of the indicated metal nitrate

Dopant 1000 ppm	Activity (mmol$_{CO}$/mol$_{Rh}$ s)	Selectivities (%)					
		methane	C$_{2+}$	C$_{1oxo}$	C$_{2oxo}$	oxo$_{tot.}$	AcH : EtOH [a]
–	31.6	76.9	8.5	0.8	13.1	14.6	no EtOH
Na	1.2	69.5	3.0	11.9	15.6	27.5	no EtOH
K	0.7	61.6	4.1	17.8	16.5	34.3	no EtOH
Ca	4.4	38.8	1.5	49.0	10.7	59.8	2.0 : 1.0
Fe	28.6	60.4	11.5	16.0	9.7	28.1	1.0 : 10.6
Al	24.4	74.6	16.7	0.7	7.6	8.7	no EtOH

[a] AcH = acetaldehyde.

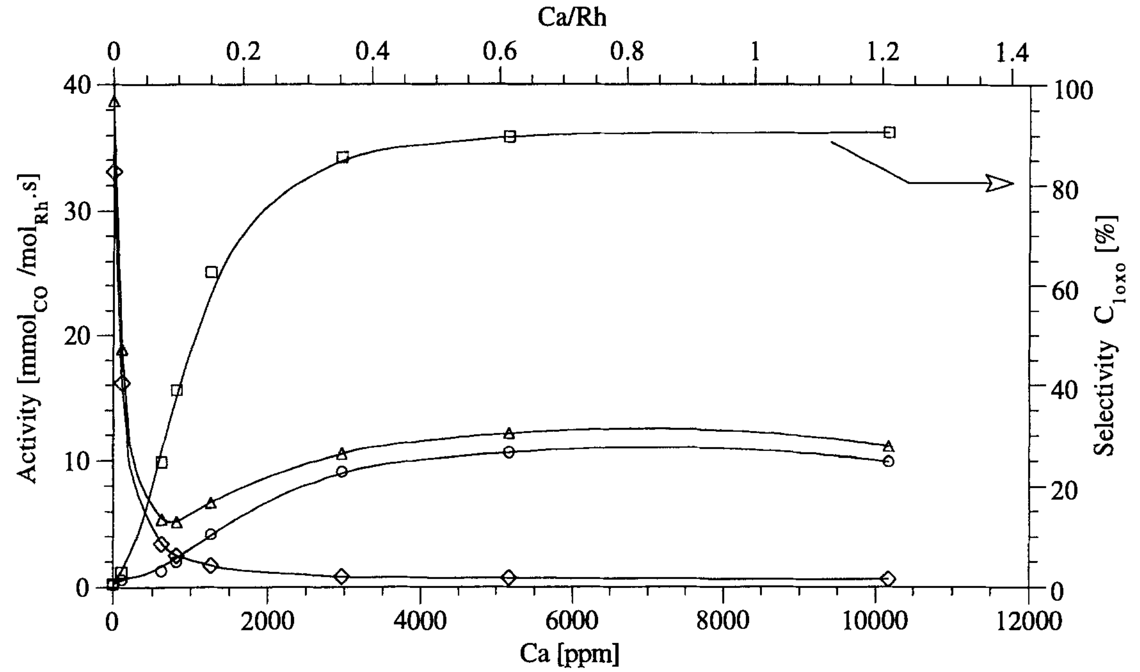

Fig. 5. Effect of the addition of Ca to Rh/SiO$_2$ catalysts prepared from Rh(NO$_3$)$_3$. (△) Total activity, (◇) activity C_{1+} hydrocarbons, (○) activity C_{1oxo}, (□) selectivity C_{1oxo}.

SiO$_2$ catalysts were used. Thus, in contrast to the Rh/X/SiO$_2$ catalysts described above, the Ca/Rh/SiO$_2$ catalysts were obtained from the same calcined Rh/SiO$_2$ precursor (prepared from Rh(NO$_3$)$_3$). Therefore they should have noble metal particles with the same number of atoms, although it is evident that the presence of promoters on the metal surface may influence the shape of the metal clusters formed after reduction.

By testing systems with different additive/noble-metal ratios, we found a clear correlation between the Ca amount and the methanol selectivity, whereas the total activity showed a more complex dependence as the result of the superposition of the exponential decrease in the activity of the hydrocarbons and the rising curve of the methanol production (fig. 5).

The promoting effect of Ca suggests that basic oxide species, close to or on the Rh particles, directly promote the methanol synthesis. The slight activity decrease at high Ca loading (Ca/Rh $\geqslant$ 0.6) is probably due to the Rh surface being covered with calcium oxide patches, as confirmed by the chemisorption measurements, e.g. H/Rh = 0.57 for the undoped catalyst, 0.48 for the Ca/Rh = 0.6 catalyst and 0.27 for the catalyst with Ca/Rh = 1.0.

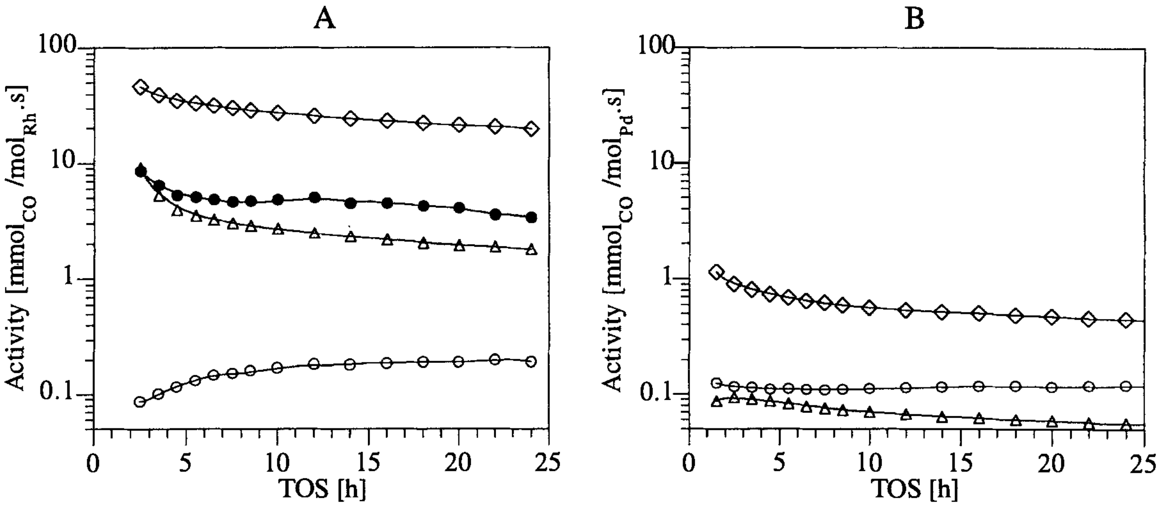

Fig. 6. Product activities in the CO hydrogenation over (A) Rh/SiO$_2$ prepared from RhCl$_3$ and (B) Pd/SiO$_2$ prepared from PdCl$_2$. (◇) CH$_4$, (△) C_{2+}, (○) C_{1oxo}, (●) C_{2oxo}.

Table 2
Comparison of the catalytic properties of methanol active catalysts

Ref.	Catalyst	Support	TOF [a] (10^{-3} s^{-1})
Poutsma et al. [38]	4.6 wt% Pd/SiO_2	Davison 57	1.8
Fajula et al. [39]	4.8 wt% Pd/SiO_2	Davison 57	27.9
Fajula et al. [39]	4.8 wt% Pd/SiO_2	Davison 01	0
Kelly et al. [40]	5.0 wt% Pd/SiO_2	Davison 03	25.2
Friedrich et al. [41]	industrial Cu/ZnO [b]	Al_2O_3	23.8
this work	5.0 wt% Pd/SiO_2	ultra pure	0.3

[a] TOF = molecules CH_3OH produced per surface metal atom per second; extrapolated to our conditions using the rate law [42] $r = kp_{H_2}^{0.75}p_{CO}^{0.15}\exp(-74404/RT)$.

[b] 493 K, 100 bar, $H_2/CO/CO_2 = 75.0/19.5/5.5$ vol%.

3.3. CO hydrogenation over Pd/SiO₂

The conversion of CO to methane, C_{2+}, C_{1oxo} and C_{2oxo} compounds on Pd and Rh catalysts as a function of time is presented in fig. 6. Whereas Rh is held to be a metal somewhere between adsorbing CO dissociatively and associatively, Pd is hardly capable of dissociating CO. Thus, the total activity of Pd/SiO_2 catalysts was almost two orders of magnitude smaller than that of Rh/SiO_2, and the product distribution was limited to methane, minor amounts of higher hydrocarbons (only C_2–C_3), and C_{1oxo} (methanol and dimethyl ether); acetaldehyde and ethanol were not formed.

In spite of the different reaction conditions, we observed a similarly low methanol activity for the Rh/SiO_2 and Pd/SiO_2 catalysts (fig. 6), indicating that Pd catalysts supported on an impurity-free SiO_2 are not particularly efficient in the methanol production, as claimed by Poutsma et al. [38] (table 2). As proposed by Fajula et al. [39] and Nonneman et al. [19,20], this suggests that impurities on the support influence the methanol activity (table 2). It also indicates that the formation of methanol through formyl intermediates plays a marginal role only.

In contrast to the Rh/SiO_2 catalysts, a dramatic influence of the salt precursor was observed for the Pd/SiO_2 catalysts. Catalysts prepared from $PdCl_2$ and $Pd(NH_3)_4(NO_3)_2$ had a higher hydrocarbon activity than when prepared from $Pd(NO_3)_2$, whereas all catalysts had a similar methanol production (table 3). This observation correlates with a strong difference in the metal dispersion (table 3). Apparently, the CO dissociation is only favoured on small Pd particles [43,44], whereas the methanol production is unaffected by the metal dispersion or by the eventual presence of chloride anions. Most likely, there is no direct influence of the metal salt anion on the catalysis, since the anion will be removed during reduction of the catalyst precursor. The anion has an indirect effect, however, through its influence on the final metal dispersion.

3.4. CO hydrogenation over Ca-doped Pd/SiO₂

As for the Rh/SiO_2 catalysts, doping of the Pd/SiO_2 catalyst with 1000 ppm Ca resulted in a strong decrease in the hydrocarbons formation, due to the suppression of the CO dissociation, and in a dramatic increase in the total activity as a consequence of the higher methanol production (fig. 7 and table 3), confirming the promoting effect of basic oxide species, close to or on the Pd particles, on the methanol formation [21,45].

The higher methanol activity of $Ca/Pd/SiO_2$ catalysts, prepared from $PdCl_2$ and $Pd(NH_3)_4(NO_3)_2$, is attributed to the higher dispersion of the Pd particles (table 3). In fact, catalysts with small noble metal particles should have greater Ca–Pd contact areas, resulting in a more efficient promotion of the methanol formation. As for the CO hydrogenation over unpromoted Pd/SiO_2 catalysts, the activity and the product distribution of the $Ca/Pd/SiO_2$ catalysts with equal Pd disper-

Table 3
Catalytic properties after 24 h of Pd/SiO_2 and $Ca/Pd/SiO_2$ catalysts

Precursor	Ca/Pd	H_{irr}/Pd	Activity ($mmol_{CO}/mol_{Pd}$ s)	TOF [a] (10^{-3} s^{-1})	Selectivities (%)		
					CH_4	C_{2+}	C_{1oxo}
$Pd(NO_3)_2$	0	0.02	0.2	8.6	12.0	2.3	85.7
$Pd(NH_3)_4(NO_3)_2$	0	0.32	0.4	0.5	54.7	3.7	41.6
$PdCl_2$	0	0.35	0.6	0.3	71.8	8.9	19.3
$Pd(NO_3)_2$	0.04	0.02	2.2	109.3	0.4	0.2	99.4
$Pd(NH_3)_4(NO_3)_2$	0.04	0.28	7.2	25.4	1.1	0.1	99.8
$PdCl_2$	0.04	0.30	6.9	22.8	0.6	0.1	99.3

[a] TOF = molecules CH_3OH produced per surface metal atom per second.

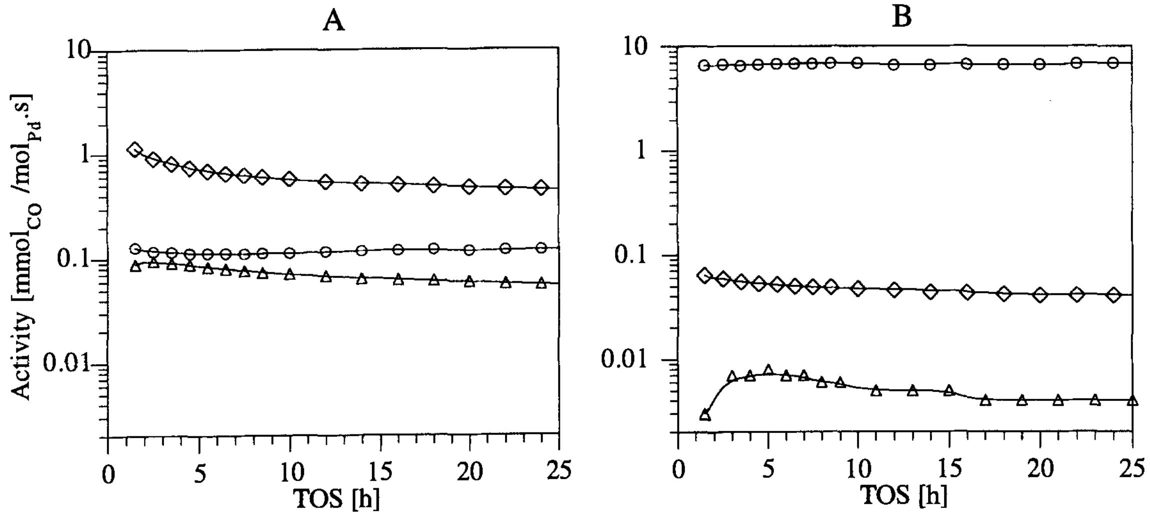

Fig. 7. Product activities in the CO hydrogenation over (A) Pd/SiO_2 and (B) Ca/Pd/SiO_2 prepared from $PdCl_2$. (◇) CH_4, (△) C_{2+}, (○) C_{1oxo}

sion was independent of the anion in the Pd precursor salt (table 3).

The variation in the activity and product distribution with the variation in the reaction temperature for hydrocarbons and C_{1oxo} formation during CO hydrogenation over a Ca/Pd/SiO_2 catalyst is shown in fig. 8. As for Rh/SiO_2 catalysts, the reaction temperature had a strong influence on oxygenate activity. Below 570 K, methanol formation is controlled by the reaction rate; temperature and C_{1oxo} activity are directly correlated (fig. 8A). On the contrary, at higher temperatures the maximal achievable yield is limited by the thermodynamic equilibrium (fig. 8B) [46–48]. In the analyzed temperature range, however, the formation of hydrocarbons is controlled only by the kinetics. Thus, hydrocarbon yields over the whole range were much lower than the maximal thermodynamic yields.

4. Conclusions

Rhodium supported on an impurity-free SiO_2 produces mainly methane, higher hydrocarbons and acetaldehyde. Differences in the behaviour of this catalyst are usually due to the presence of contaminants on the support. They can be easily transferred close to or onto the metal surface during the catalyst preparation and affect the catalytic properties. But, as observed by Burch and Petch [23], contamination with metals may occur even during the reaction. Thus, the use of a quartz reactor and of a trap upstream from the catalyst is recommended in order to avoid deposition of Fe, Ni or Cr carbonyls on the metal surface.

There is no apparent dependence of the catalytic properties of Rh/SiO_2 catalysts on the precursor salt (nitrate or chloride) used during impregnation. Thus,

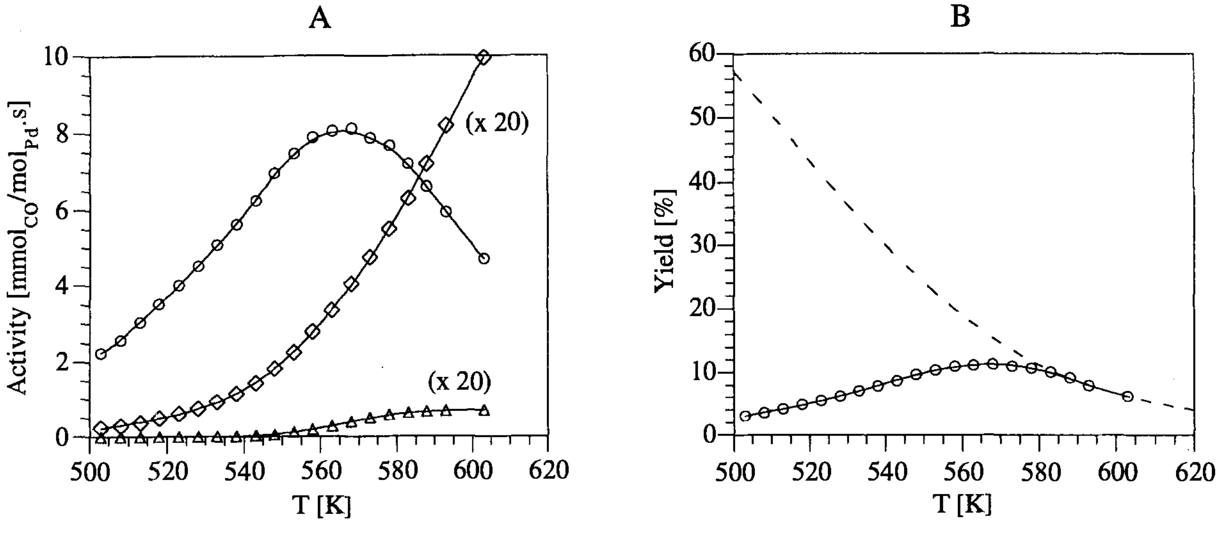

Fig. 8. The effect of reaction temperature in the CO hydrogenation over Ca/Pd/SiO_2 prepared from $Pd(NH_3)_4(NO_3)_2$. (A) Product activities: (◇) CH_4, (△) C_{2+}, (○) C_{1oxo}; (B) (○) C_{1oxo} yield, (– – –) thermodynamic yield.

the eventual presence of residual anions on the noble metal surface does not have an effect on the activity or on the product distribution.

The reaction temperature has a dramatic influence on the behaviour of CO hydrogenating catalysts and particularly on their activity towards oxygenates. In order to perform accurate and comparable activity tests, unintentional variation in the reaction temperature due to excessive heat production must be avoided. Differential conditions (1–5% conversion) and a careful control of the effective temperature of the catalytic bed are, therefore, absolutely necessary.

Rh and Pd catalysts, supported on impurity-free SiO_2, have similarly low methanol activities. Contradictory to the claim made by Poutsma et al. [38], Pd is clearly not a good methanol catalyst. This may suggest that, although formyl species were detected by chemical trapping on the metal surface [49,50], these adsorbates play no relevant role in the methanol formation. The higher C_{1oxo} selectivity of the Pd/SiO_2 catalyst is only a consequence of the low hydrocarbons formation due to the modest CO dissociation capacity.

The intentional doping with alkali as well as alkaline earth oxides leads to a strong suppression of the CO dissociation and consequently to a decrease in the methane and C_{2+} formation. The presence of basic promoters, like Ca, close to or on the active metal particle, has a strong promoting effect on the methanol production. Furthermore, the clear correlation between Ca amount, noble metal surface and C_{1oxo} activity may confirm that the formation of methanol occurs through formate intermediates, formed by the reaction of CO with the basic support surface or at the interface between the promoter oxide and the noble metal particle. Indeed, methylformate used to be produced industrially by reacting CO and methanol over sodium and calcium hydroxide [51].

Supporting evidence for our hypothesis comes from the FTIR detection of formate species on catalysts promoted by basic oxides [4,16,17,32], and more recently from the work of Joo et al. [52] about the hydrogenation of Cu- and Zn-formate.

The differences in the methanol activities between high and low dispersed $Ca/Pd/SiO_2$ catalysts may be attributed to the differences in the extension of the Ca–Pd interface. Thus, catalysts with small Pd particles have a large Ca–Pd contact surface and, therefore, promote the formate formation better. Surface science studies with Rh and Pd foils covered with CaO are in progress to prove this point.

Acknowledgement

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