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FTIR Study of the Adsorption of Methanol on Clean and Ca-Promoted Pd/SiO_2 Catalysts

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The adsorption and decomposition of methanol on a highly dispersed supported Pd/SiO_2 catalyst (2% Pd w/w) prepared via ion exchange of $[Pd(NH_3)_4]^{2+}$ in alkaline solution, together with two Ca-promoted preparations (Ca/Pd = 2 at/at), where calcium was added either to the prereduced Pd crystallites or to the diammine palladium complex, were studied by FTIR at 298–623 K. Methanol adsorbs *and* reacts at 298 K on Pd/SiO_2. The presence of Pd on the silica surface influences slightly the processes occurring on the support, where CH_3OH is mostly adsorbed molecularly at room temperature, but readily forms very stable Si–O–CH_3 groups upon heating. The dissociation of methanol via both O–H and C–O bond breaking is observed on Pd. The latter scission is only detected at 653 K. At room temperature, adsorbed CH_3OH decomposes easily on the Pd crystallites, to give CO multicoordinated to the metal surface. Formyl species were also found at this temperature, but they promptly disappeared, above 393 K, when the catalyst was heated. Calcium promotion, either to the prereduced Pd or to its diammine complex precursor during the preparation steps, enhances methanol decomposition onto the catalyst surface, even at room temperature. With heating, formyl groups are replaced by mono- and bi-dentate formate species, which are chemisorbed on the support and/or the promoter. Bidentate formate is not as stable as the monodentate form and its IR band vanishes above 500 K. The observed features indicate that an excellent Ca–Pd intimacy was achieved with both types of promotion strategies.

Key Words: **syn-gas conversion; CO_2 hydrogenation; FTIR spectroscopy; supported palladium; calcium promotion; methanol adsorption.**

INTRODUCTION

Supported palladium has been shown to be highly selective in CH_3OH synthesis, via the hydrogenation of both carbon oxides, CO and CO_2 (1). Yet, on pure or well-purified silica the catalytic activity of Pd/SiO_2 is rather modest, quite similar to that of Pd black (2, 3).

Controlled addition of a suitable promoter, such as Ca, can dramatically enhance the catalytic activity of the system *and* its selectivity to methanol (3–6). So, for instance, by adding calcium acetate or calcium nitrate (decomposable salts that will not lead to anionic promotion) to air-precalcined Pd/SiO_2, reaction rates up to 25–40 times higher than with the unpromoted catalysts were achieved, using syn–gas mixtures at usual process conditions (3, 4). Furthermore, these research teams have found that the selectivity to methanol improved at higher Ca/Pd ratios (better than 92%), albeit reaching a plateau above calcium-to-palladium ratios which were dependent on the catalyst preparation procedures.

The mechanism of methanol synthesis from CO–CO_2–H_2 mixtures over promoted Pd catalysts remains uncertain. Therefore, current studies aim at improving the understanding of why the promoters are effective and, in particular, where they are located. Among these studies, an evaluation of the nature of the methanol reaction intermediates can provide important insight into the mechanism of the synthesis and, to this end, the present work examines the adsorption and reaction of CH_3OH on pure and Ca promoted Pd/SiO_2 by means of FTIR spectroscopy.

EXPERIMENTAL

A highly dispersed supported Pd/SiO_2 catalyst (2% Pd w/w), together with two Ca-promoted preparations (Ca/Pd = 2 at/at) and the corresponding blanks of pure and calcium-loaded silica were used in this FTIR study (See Table 1).

The catalysts were made by ion-exchanging palladium acetate (Engelhard, 99.5% w/w) in aqueous ammonia (pH 11) onto the prepurified, calcined support. The support, a mesoporous silica (Davison G59: BET surface area = 254 m^2/g, modal radius = 83 Å), was purified by organic and inorganic washing (7). After air drying, the anchored Pd tetraammine complex was decomposed to the diammine one at 423 K. Part of the stock was used as such, to prepare a first type of Ca-promoted catalysts (S code), where

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TABLE 1

Characteristics and Codes of the Catalysts

Catalyst type[a]	Pd loading (% Pd w/w)	Ca loading (% Ca w/w)	Ca/Pd (at/at)	FE[b]	d_p (TEM)[c] (Å)	Code
R	2	1.5	2	0.65	1.4	MR5
S	2	—	0	0.75	1.5	MS0
	2	1.5	2	0.41	1.4–3.5[d]	MS5
Blank		1.5	NA			BS5
		—	NA			SiO_2

[a] Support: Davison G59 silica, mesoporous ($S_g = 254$ m^2/g, modal radius = 83 Å).

[b] Fraction of exposed Pd (Hydrogen chemisorption). Chemisorption stoichiometry: $H_{ad}/Pd_s = 1$ (9).

[c] Average volume-to-surface particle diameters determined by transmission electron microscopy, where $d_p\ (\mathrm{TEM}) = \sum n_i d_i^3 / \sum n_i d_i^2$ (5, 8).

[d] Bimodal distribution.

maximum Ca–Pd interaction was expected, while a second part was H_2 prereduced instead (723 K, 2 h, heating rate: 2 K/min), to minimize said interaction (R code). Calcium acetate (AESAR-J. Matthey Puratronic, 99.9965%; Bi, Cu, Fe, Mg, and Na metal traces <1 ppm ea.) was added by pore volume impregnation, *in vacuo*, to each material and then water was sublimated. Finally, the catalysts were calcined at 673 K (2 h, heating rate: 2 K/min) in dry, CO_2-free air and reduced in H_2 at 723 K. Further details about the catalyst preparation procedure are given elsewhere (5, 8).

For IR measurements, the dried powders were pressed into self-supporting wafers (10 mg/cm^2; applied pressure: 5 ton/cm^2) and placed in a portable Pyrex cell with water-cooled NaCl windows. The cell could be heated up to 673 K and was attached to a conventional high-vacuum system (base pressure = 10^{-6} Torr; 1 Torr = 133.3 N m^{-2}) equipped with a manifold for gas flow, which permitted performing all pretreatments and measurements *in situ*.

The catalysts and blanks were reduced in H_2 for 60 min at 523 K (100 cm^3/min, heating rate: 2 K/min), after a previous purging with N_2 for 15 min at 298 K. Then, the chemisorbed hydrogen on Pd was eliminated by evacuating the cell for 120 min, at 653 K (heating rate: 10 K/min). Finally, the samples were cooled to 298 K (hereafter: room temperature, or RT). IR spectra of the "clean" wafers were taken during this cooling process for further use.

Methanol (Carlo Erba RPE-ACS-ISO-For analysis, 99.9%), purified by a series of freeze–thaw cycles under vacuum to remove disolved gases and stored in a glass bulb attached to the manifold, was dosed (1 Torr) into the cell at RT. The catalyst sample was kept under these conditions for 30 min; spectra were taken every 5 min. Next, the temperature was raised to 653 K (heating rate: 3 K/min), with additional IR spectra taken every 20 K. Then, the cell was evacuated to 3×10^{-5} Torr; intermediate spectra were recorded at 1, 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4} Torr. Finally, the temperature was lowered to 523 K and hydrogen was admitted into the cell and flown through the sample wafer (60 cm^3/min) to record the reactive behavior, or desorption, of any species that might have remained after the evacuation at high temperature. For comparison purposes, infrared spectra of gaseous CH_3OH (1 Torr) were also taken.

The spectra were recorded with a single beam Shimadzu 8001 Fourier Transform IR spectrometer ($R = 4$ cm^{-1}; 100 scans per spectrum). They were processed as follows: Background spectra of the clean samples (obtained at each temperature) were subtracted. Background noise correction and Gaussian deconvolution of bands—whenever possible—were done on digitalized spectra by means of commercial software (Microcal Origin 4.1, w/Peak Fitting Module).

Gas sources were N_2 99,999% (Scott U.P.G.) and H_2 99.999% (Scott U.P.G.), purified to remove water and O_2 with 3-Å molecular sieve (Fisher Co.) and MnO/Al_2O_3 cartridges, respectively.

RESULTS AND DISCUSSION

Adsorption of Methanol on Pd/SiO$_2$

The adsorption of gaseous methanol on the clean Pd/SiO_2 catalyst at room temperature is a fairly fast process. After 30-min exposure to 1 Torr CH_3OH the spectral features very much resembled the initial features, as shown in Fig. 1. In the C–H stretching region several bands appeared at 2997, 2953, 2925, and 2848 cm^{-1}. The signals at 2953 and 2848 cm^{-1} correspond, respectively, to the $\nu_{as}(CH_3)$ and

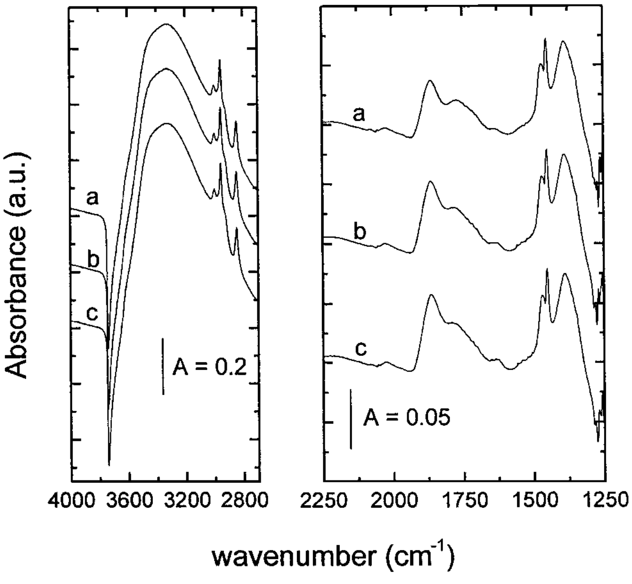


FIG. 1. FTIR spectra of methanol (1 Torr) adsorbed on Pd/SiO_2 at 298 K for: (a) 0.5 min, (b) 15 min, and (c) 30 min. The sample was prereduced *in situ* under flowing H_2 (100 cm^3/min) at 523 K for 1 h (at 2 K/min), then evacuated at 653 K for 2 h (at 10 K/min) and cooled down to RT.

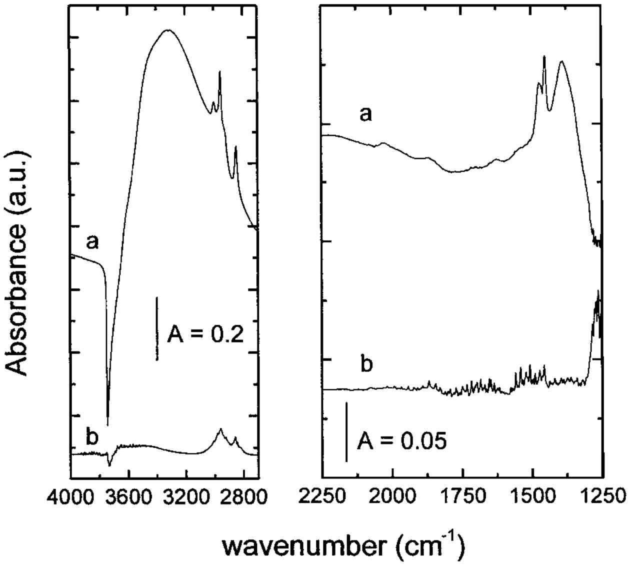


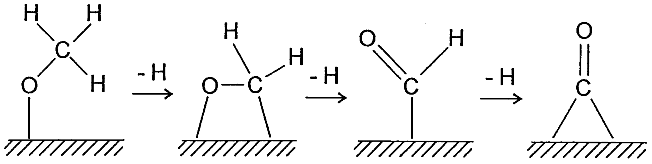
FIG. 2. Infrared spectra of methanol (1 Torr) adsorbed on SiO_2 at (a) 298 K, 30 min and (b) 653 K, 30 min. The sample was pretreated as described in Fig. 1.

$\nu_s(CH_3)$ of molecularly adsorbed methanol, with their P (low frequency) and R (high frequency) bands well differenciated for the asymmetric stretching vibration. The remaining, weak $\nu(CH)$ signals have also been positively identified as typical of CH_3OH physisorbed onto silica at RT (10), as well as the additional bands appearing at lower wavenumbers: 1471 [$\delta_{as}(CH_3)$], 1447 [$\delta_s(CH_3)$], and 1391 [$\delta(OH)$-in plane] cm^{-1}. All these signals are slightly shifted toward higher frequencies with respect to those of methanol in gas phase, which is characteristic of methanol physisorbed onto this support (11, 12) (see also Fig. 2, upper trace.)

The basic difference between the spectra on silica and on the Pd/SiO_2 catalyst is that for the support no absorption bands were registered in the 1700–2200 cm^{-1} range (Fig. 2). However, methanol decomposes on the Pd/SiO_2 catalyst at 298 K, to give several bands at 2023(vw), 1863 (broad, convoluted), and 1748 cm^{-1}. The absorbance of these signals increased with time: they all grew by about 35% after 30-min exposure, indicating that the decomposition process is kinetically controlled at room temperature.

The first of these decomposition bands correspond to carbon monoxide, which easily chemisorbs on Pd (CO_s) at ambient temperature. In general, two well-reported types of CO_s on palladium are identified. Bands above 2000 cm^{-1} are attributed to terminal, mono-coordinated or linearly bonded CO (CO_L), while the broad, convoluted bands under 2000^{-1} are assigned to multicoordinated, bridging CO. The latter have been further classified from single-crystal studies as CO_{B1}, corresponding to di-coordinated bridging CO on structurally open crystal planes such as (100) or (210), close to 1970 cm^{-1}, CO_{B2}, corresponding to di-coordinated bridging CO on Pd(111), around 1956 cm^{-1} and a band below 1830 cm^{-1} usually assigned to triply bridging CO on Pd(111) "hollow" sites (hereafter CO_H). On supported palladium these bands locate at lower frequencies than on Pd single crystals (13–16).

Our data indicate that methanol decomposes at 298 K on the palladium crystallites to give mostly multicoordinated CO_s, as was also found by Solymosi and coworkers (12). The reaction pathway probably starts with the (easy) scission of the O–H bond of CH_3OH to give atomic hydrogen and adsorbed methoxy, which is then dehydrogenated:



SCHEME 1

The first step in this dehydrogenation process seems to be facilitated because the chemisorbed methoxy species is orientated with its O–C axis tilted to the surface since, as shown below, the relative intensity of the $\nu_{as}(CH_3)$ and $\nu_s(CH_3)$ signals is very similar (10, 17–19). The band at 1748 cm^{-1} corresponds to the CO stretching of formyl groups (HCO) chemisorbed onto the palladium metal (20). (The $\nu(CH)$ signal of the HCO group is usually weak and overlapped with the methyl bands of the methoxy group.) Formyl groups, and adsorbed formaldehyde, have been postulated as surface intermediates in the catalytic decomposition of methanol on Pd and Cu catalysts (21–24).

The spectral features in the OH region reveal extensive hydrogen bonding, as shown by the broad band centered about 3435 cm^{-1} and the intense negative peak at 3742 cm^{-1}, which indicates that isolated OH groups of the silica are consumed. These isolated hydroxyl groups are left on the silica after the high temperature evacuation pretreatment. Unlike the case of pure silica, fewer free hydroxyls were consumed on Pd/SiO_2, probably because part of the dosed methanol was decomposed rather than just chemisorbed.

Figure 1 also shows that a small absorption band appears at 1620 cm^{-1}. This signal is assigned to the $\delta(HOH)$ mode of adsorbed *molecular* water, most likely condensing from the decomposition of the alcohol as

$$CH_3OH + OH \rightarrow CO + H_2O + 3/2\,H_2. \qquad [1]$$

Upon heating at progressively higher temperatures the intensity of the bands in the CH stretching region decreased noticeably, and the dosed methanol further reacted to give more CO (Fig. 3). Aside from the reactivity of the adsorbate on Pd, most of the spectral features in this region gave a pattern similar to the behavior of CH_3OH on the silica support: At approximately 353 K, the band at 2848 cm^{-1}

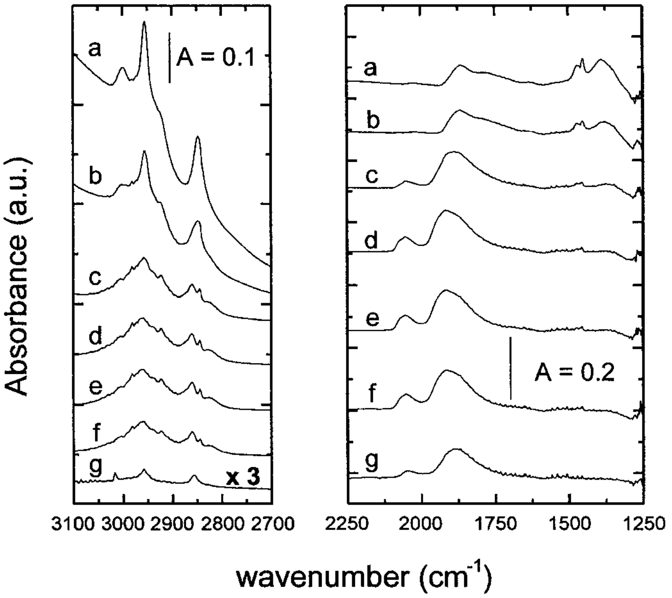


FIG. 3. FTIR spectra of methanol (1 Torr) adsorbed on Pd/SiO_2 at increasing temperatures: (a) 298 K, 30 min, (b) 333 K, (c) 373 K, (d) 413 K, (e) 453 K, (f) 493 K, (g) 653 K, 30 min. The sample was pretreated as described in Fig. 1.

shifts to 2856 cm^{-1} and, at the highest heating temperature, only two small bands with maxima located at 2957 and 2857 cm^{-1} can be distinguished.

These last two bands correspond to methoxy group chemisorbed onto silica, which can form onto this solid above 253 K, but cannot be removed from it by simply heating (11, 12). Its presence was masked in the spectra recorded during adsorption at RT. (As shown by Barteau and coworkers, OCH_3 species can form onto palladium planes, but desorb from the metal at low temperature (25).) This process of formation of chemisorbed methoxy groups onto silica proceeds with the concomitant, progressive disappearance of the bands at 3470 and 1390 cm^{-1}, assigned to ν(OH) and δ(OH), respectively. The rest of the low frequency bands can no longer be discerned at 653 K in either the catalyst or the support (Figs. 1 and 2, lower traces). On this highly dispersed Pd/SiO_2 catalyst, then, the presence of Pd contributes only slightly to the absorption of molecularly and dissociatively chemisorbed methanol detected by IR on the silica support.

The integrated intensity of the ν(CO) signals of carbon monoxide chemisorbed onto Pd grew up to 393 K and became progressively smaller at higher temperatures, where the desorption of CO was faster than methanol decomposition. This maximum agrees well with the desorption maxima of chemisorbed CO (400 K) reported by different authors for either Pd or Rh (26, 27).

Multicoordinated CO_s was the preferred species on the surface at low temperatures; mono-coordinated CO was not observed below 353 K. In addition, the ν(CO) of all these bands shifted noticeably with the heating. This shift can be attributed both to changes in the preferred adsorption forms and relative stability with temperature of the different adsorbed modes of carbon monoxide and to dipole–dipole coupling (13, 16). With desorption, the latter becomes less important and generally causes a red shift. The signal of molecular CO in the gas phase of the closed cell (2143 cm^{-1}) was already detectable above 473 K and, conversely, the intensity of the HCO band became almost negligible the higher the temperature was. This is in complete agreement with former work, reporting that formyl species adsorbed on Pd or Pt are highly unstable upon heating (20, 28, 29).

Together with these changes, brought about by the decomposition of chemisorbed methanol sketched in Scheme 1, a new signal located at 3016 cm^{-1} was observed at high temperature (653 K), which disappeared immediately upon evacuation (Figs. 3 and 4). The signal is assigned to CH_4 in gas phase, the preferred product of methanol decomposition and/or synthesis at low pressure (30). Single-crystal studies have shown that the scission of CH_3OH to give chemisorbed CH_3 and OH moieties can only proceed on Pd(111) surfaces (31). So, on the small, supported polycrystalline Pd particles of our catalyst, the rupture of both the O–H and C–O bonds can occur.

The free OH groups of the silica surface, lost during exposure to the adsorbate at room temperature, can regenerate almost entirely upon heating. At 653 K, 96% of these hydroxyls were recovered on Pd/SiO_2, *versus* 98% on the pure silica (Figs. 2 and 4).

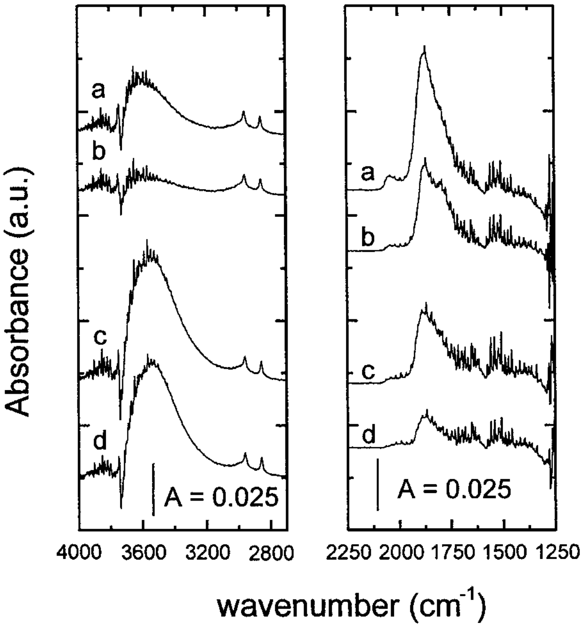


FIG. 4. Desorption of methanol from Pd/SiO_2 at 653 K: (a) 10^{-1} Torr, 30 min, (b) 10^{-4} Torr, 30 min, followed by reaction with flowing H_2 (100 cm^3/min) at 523 K for (c) 0.5 min, (d) 40 min.

Right after heating, the catalyst was evacuated. At this rather high temperature (653 K) the remaining, chemisorbed methoxy groups attached to silica (2957, 2857 cm^{-1}) showed to be very stable and, after 30 min at 3×10^{-5} Torr, these bands were almost as intense as at the beginning of the evacuation process (Fig. 4). Raskó *et al.* have analyzed in depth the high thermal stability of methoxy groups on silica and have concluded that the irreversible adsorption of methanol on SiO$_2$ occurs to a greater extent the higher the temperature at which the solid is degassed (12, 32).

Carbon monoxide is still strongly chemisorbed onto Pd at 653 K, but most of the CO$_L$ is promptly eliminated under vacuum (33, 34). Figure 4 also shows that the chemisorbed CO readily reacts with flowing H$_2$ and that some water is formed in the process, probably because the reaction mostly leads to methane under these conditions (high H$_2$/CO ratio and low pressure,) at this temperature:

$$CO + 3\,H_2 \rightarrow CH_4 + H_2O. \qquad [2]$$

Nevertheless, the residual methoxy groups could not be removed by the hydrogen treatment, most likely because water coming from Reaction [2] does not chemisorb onto silica at high temperature and, so, is unable to hydrolyze the Si–O bond.

Adsorption of Methanol on Ca-Doped Prereduced Pd/SiO$_2$

Figure 5 displays the spectra obtained on dosing methanol (1 Torr) at 298 K on the Ca-doped *prereduced* Pd/SiO$_2$ catalyst (coded MR5). In general terms, the exposure caused the appearance of the same bands of intact methanol (whether molecularly adsorbed or chemisorbed as methoxy) as in the Ca-free Pd/silica, although with somewhat lower intensities. The bands ascribed to methanol physisorbed onto the support, namely: stretchings and bendings of the –CH$_3$ and –OH groups, located at frequencies identical to that on the pure silica and/or the unpromoted catalysts. Yet, after 30-min exposure some gaseous CH$_3$OH could still be observed, as revealed by the P branch of the ν_{as}(CH$_3$) vibration mode of molecular methanol at 2970 cm^{-1} and the characteristic ν(CO) bands at 1055(P), 1030(Q), and 1011(R) cm^{-1} (not shown).

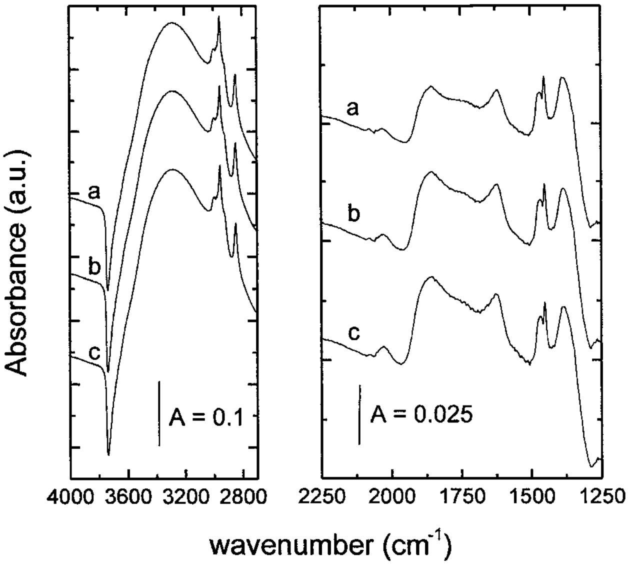


FIG. 5. Infrared spectra of methanol (1 Torr) adsorbed on MR5 (Promoted Ca–Pd/SiO$_2$; calcium added to prereduced Pd metal particles; Ca/Pd = 2 at/at) at 298 K, for (a) 0.5 min, (b) 15 min, and (c) 30 min exposure. The sample was pretreated as indicated in Fig. 1.

At room temperature, methanol decomposed on the promoted catalyst as well, but showed several differences with the clean Pd/SiO$_2$ sample: The band assigned to the stretching vibration of the carbonyl group of formyls chemisorbed onto the Pd metal crystallites [ν(CO) = 1748 cm^{-1}] became almost as important as the bridged forms of chemisorbed CO, suggesting (see Scheme 1) that the complete dehydrogenation of methanol is less favored on the Ca-promoted catalyst. In addition, some on-top CO$_L$ was found and—in comparison with Pd/SiO$_2$—more multiple-bonded CO$_s$ species were observed. Finally, it is worth mentioning the broad background shoulder/band in the 1850–1650 cm^{-1} region, which has been reported to include a contribution owing to a convoluted band of adsorbed CO bonded to Pd with the carbon atom, while the oxygen atom is bonded to a promoter metal cation (35–37). So, this “background” signal might well be the fingerprint of Ca–Pd intimacy of the catalyst.

Interestingly, the δ(HOH) band of adsorbed water at 1623 cm^{-1} was more intense on the Ca-doped catalyst, *but* the loss of free OH groups on the support was about 30% of that on Pd/SiO$_2$. We believe that these features are related to the presence of CaO$_x$H$_y$ in the vicinity of the palladium crystallites, which can retain part of the water formed via Reaction [1], thus preventing the annihilation—at least partially—of free hydroxyl groups on the silica surface.

Upon heating, the reactivity of the sorbed CH$_3$OH was also different on this promoted catalyst (Fig. 6). More –OCH$_3$ groups were formed on MR5 than on Pd/SiO$_2$ (with the characteristic shift from 2848 to 2856 cm^{-1} and disappearance of the ν(CO) and δ(OH) bands). These metoxys were also more stable, a feature found by Solymosi and co-workers on K-doped Pd/SiO$_2$ (12).

Nevertheless, the broad band of CO$_s$ showed about the same qualitative and quantitative changes: The terminal (CO$_L$) and CO$_{B1}$ chemisorbed forms increased the most up to 400 K and, at higher temperatures, the CO$_L$ desorbed preferentially. The remaining bridged CO then experienced a shift toward lower wavenumbers, when the dipole–dipole interactions became smaller (26). Also, above 433 K gaseous methanol could no longer be seen (while the low frequency CH$_3$OH$_{(g)}$ bands were evident on Pd/SiO$_2$ even

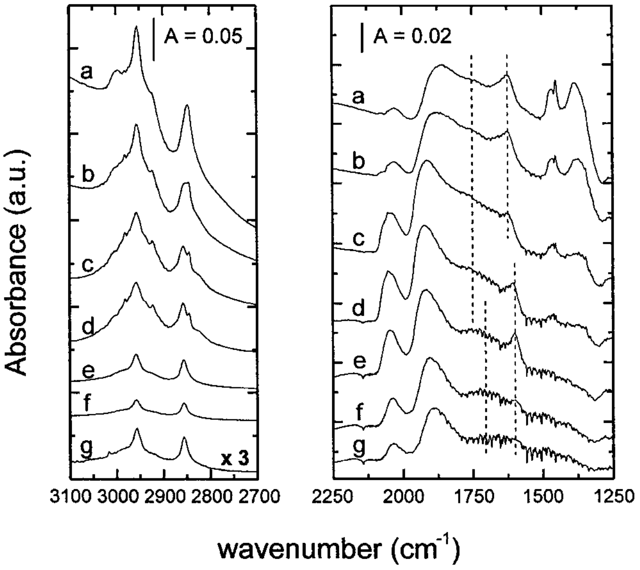


FIG. 6. Spectra of methanol (1 Torr) adsorbed on MR5 at increasing temperatures: (a) 298 K, 30 min, (b) 333 K, (c) 373 K, (d) 433 K, (e) 493 K, (f) 573 K, and (g) 653 K, 30 min. The sample was pretreated as indicated in Fig. 1.

at 473 K), at which point $CO_{(g)}$ features already became evident.

Together with the temperature increase, the signal at ca. 1750 cm^{-1}, assigned to the formyl (HCO) and H_2CO groups, disappeared progressively. From 373 K onward, a new band at 1705 cm^{-1}, with an absorption maximum at 573 K, indicates that monodentate *formate* groups (hereafter, m-HCOO) were formed on the surface instead (37). At about 500 K another signal, located at 1598 cm^{-1}, showed its maximum height. This band was the only band that could be seen—in tiny amounts—on the blank of Ca/SiO_2 (see Fig. 7), and it corresponds to the $\nu_{as}(OCO)$ vibration of a chemisorbed bidentate formate species (b-HCOO). This frequency of vibration is almost independent of the adsorbent, as has been extensively reported (12, 20, 38–44).

It is interesting to compare these features with some results on the adsorption and decomposition of methanol obtained by Waugh and coworkers (10) using a model Cu/SiO_2 catalyst. Infrared spectra of methanol adsorbed at 295 K on reduced Cu/SiO_2, and on Cu/SiO_2 that had been preoxidized, were reported. Methanol was chemisorbed on reduced Cu/SiO_2 to give methoxy species on both silica and copper; it gave a trace of formate on copper via reaction with residual surface oxygen and was weakly adsorbed at SiOH sites on the silica support. Heating the adsorbed species at 393 K led to the loss of methoxy groups on copper and the concomitant formation of bidentate surface formate. The reactions of methanol with oxidized Cu/SiO_2 were similar to those for the reduced catalyst although surface oxygen promoted the formation of surface methoxy groups on copper. Subsequent heating at 393 K led first to monodentate formate before the appearance of bidentate formate.

It seems, then, that during the decomposition of CH_3OH on MR5 at increasing temperatures, the intimacy or decoration of CaO_xH_y on the Pd crystallites helps in the buildup of surface formate species, of which the monodentate one seems, thermally, more stable.

Like on the pure Pd/SiO_2, traces of methane in the gas phase ($\nu(CH_4) = 3016$ cm^{-1}) were produced by the MR5 catalysts at 653 K, showing evidence of some scission of the CO bond. Even though our IR signals are too weak to be conclusive, the addition of basic metal oxides as cocatalysts in the conversion of synthesis gas to methanol on supported palladium catalysts has been shown to inhibit CO dissociation (3) and, so, it is not unexpected to have smaller CH_4 peaks on MR5 than over the Pd/SiO_2 catalyst.

Adsorption of Methanol on Ca-Doped Pd–diammine/SiO_2

The overall spectral features after the exposure of 1 Torr methanol at RT to the other promoted catalyst, MS5 (in which $Ca(AcO)_2$ was added prior to decomposing the palladium diammine complex), were quite similar to those the prereduced preparation, MR5. Yet, although the IR spectrum in the $-CH_3$ stretching region was almost identical, the decomposition of methanol to give chemisorbed CO was less pronounced on MS5 (Figs. 5 and 8). Also, less CO_{B1}, di-coordinated on the structurally open Pd(100) crystal planes, was found and the linear-to-bridging (L/B) ratio was smaller than on MR5. These features are consistent with our hydrogen chemisorption and TEM data, which showed that

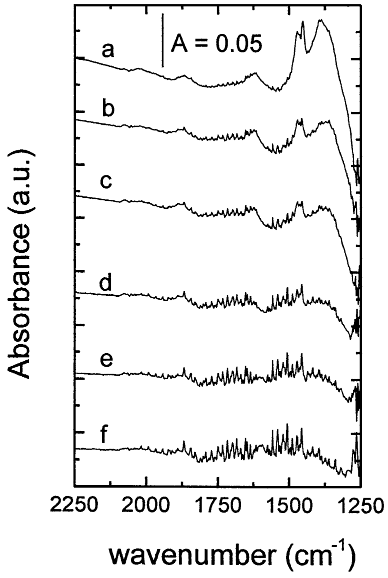


FIG. 7. Infrared spectra of methanol (1 Torr) adsorbed on BS5 (blank of Ca/SiO_2) at increasing temperatures: (a) 298 K, 30 min, (b) 333 K, (c) 373 K, (d) 473 K, (e) 573 K, and (f) 653 K, 30 min. The sample was pretreated as indicated in Fig. 1.

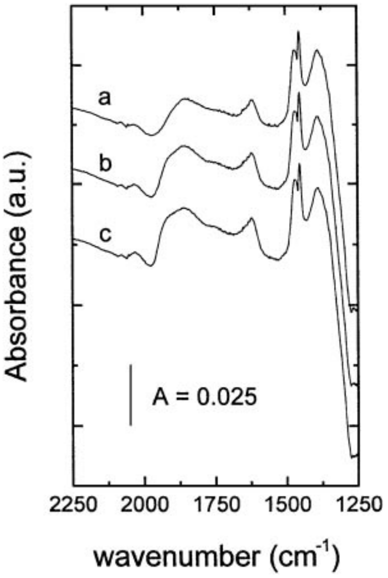


FIG. 8. Infrared spectra of methanol (1 Torr) adsorbed on MS5 (Promoted Ca–Pd/SiO$_2$; calcium added to nonreduced Pd metal particles; Ca/Pd = 2 at/at) at 298 K, for: (a) 0.5 min, (b) 15 min, and (c) 30 min exposure. The sample was pretreated as indicated in Fig. 1.

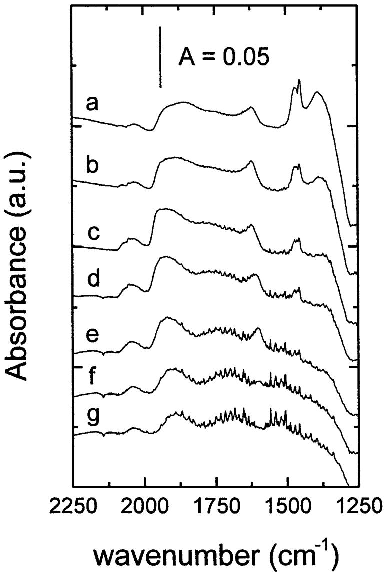


FIG. 9. Spectra of methanol (1 Torr) adsorbed on MS5 at increasing temperatures: (a) 298 K, 30 min, (b) 333 K, (c) 373 K, (d) 433 K, (e) 493 K, (f) 573 K, and (g) 653 K, 30 min. The sample was pretreated as indicated in Fig. 1.

the exposed metal fraction was smaller in the MS5 catalysts and, additionally, that the particle size of the Pd crystallites was larger (Table 1). As it is well known, linear CO is preferentially formed on low-coordinated Pd atoms. This fact immediately implies that the L/B ratio of chemisorbed CO forms should decrease with increasing particle size of the metal crystallites, because large particles expose a smaller fraction of low-coordinated (corner or edge) atoms than small particles, if all other factors are kept equal (13).

The effect of heating upon the adsorbed species was very similar in the two types of Ca-promoted catalysts, both in the methoxy and the carbonyl-related IR regions. Figure 9 shows that, again, the formyl signal appeared at 1745 cm^{-1}, slightly differentiated from the broad convoluted band of the chemisorbed CO bands (CO$_L$ = 2042 cm^{-1}; CO$_B$ = 1896 cm^{-1}). As already mentioned, formyl groups become unstable with heating and, so, this HCO signal could no longer be distinguished at higher temperatures: Above 573 K, a band located at 1700 cm^{-1} (assigned to m-HCOO) replaced it as the main feature in this spectral region, together with some remaining linear and bridge-bonded CO. The higher heterogeneity of the Pd crystallites, proper of their bimodal distribution on this catalyst, is nicely shown during the heating process: chemisorbed CO$_L$ and CO$_B$ show convoluted but distinct bands associated with the (111) and (100)—or more open—planes (45).

Like on MR5, bidentate formate was formed on MS5 (onset at ca. 433 K, 1598 cm^{-1}), with a maximum at about 500 K as well. *However*, these species were noticeably more abundant and vacuum-stable on the prereduced Ca-promoted palladium catalyst (Fig. 10). Concurrently, at high temperature (653 K) the remaining chemisorbed CO was also much more stable on MR5 than on MS5 and, upon evacuation, hardly any carbon monoxide was left on the latter. Regardless, much less chemisorbed CO remained in either of the promoted catalysts as compared with the clean Pd/SiO$_2$,

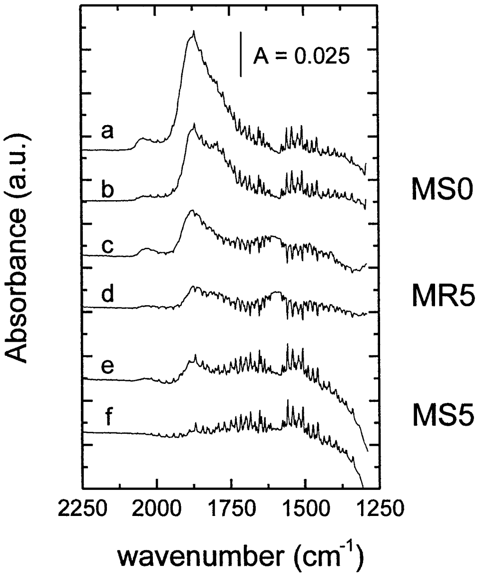


FIG. 10. Desorption of methanol from Pd/SiO$_2$ and Ca-promoted Pd/SiO$_2$ catalysts at 653 K: MS0, (a) 10^{-1} Torr, (b) 10^{-4} Torr, 30 min; MR5, (c) 10^{-1} Torr, (d) 10^{-4} Torr, 30 min; MS5, (e) 10^{-1} Torr, (f) 10^{-4} Torr, 30 min.

which suggests that Ca–Pd intimacy might well be the unifying explanation of these observed differences (46).

Regarding the methoxy groups onto the silica support, both promoted catalysts gave identical spectra as on the SiO_2 and the unpromoted Pd/SiO_2 after the heating/evacuation procedures. Finally, on MS5 the methane signal at 3016 cm^{-1} was barely appreciable at the highest temperature used, 653 K.

After evacuation, the exposure of the remaining chemisorbed species on MR5 and MS5 to flowing H_2 at 523 K brought about the same minor changes formerly observed on the clean Pd/SiO_2: At this temperature, only the production of methane prevails at atmospheric pressure, owing to thermodynamic constraints and, under flow of hydrogen, CH_4 can easily be removed from the cell.

The observed features indicate that an excellent Ca–Pd intimacy was achieved with both types of promotion strategies. Also, taking into consideration the principle of microscopic reversibility, the enhanced decomposition of the adsorbate on these $Ca–Pd/SiO_2$ catalysts significantly correlates with their improved catalytic activity in the selective hydrogenation of carbon monoxide to methanol.

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