XPS / SIMS studies of the promoter action in methanol synthesis over silica-supported Pd catalysts

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Pd-based catalysts prepared from ultra-pure SiO_2 and doped with 5000 ppm Li, Ca and La were subjected to CO hydrogenation ($H_2/CO = 2$, $p = 9$ bar, $T = 553$ K) in a flow reactor directly attached to an ultra-high vacuum chamber with facilities for X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). The catalysts exhibited high selectivity (usually above 99%) for methanol synthesis and their activities were found to increase in the order Li < Ca < La. Subsequent analysis by SIMS revealed the presence of surface formate and methoxy on the silica support. No such species were found to be bound to the Pd particle surface. These conclusions are based on the detection of COO(H) and $SiOCH_3$ ions while respective Pd-based species were absent from the mass spectra. This indicates a mechanism to be in operation in which hydrogen is activated on Pd metal and subsequently spilled over to the support in order to react with formate to methanol. XPS studies of SiO_2 samples containing 10 wt% of Ca, in the absence of Pd metal, demonstrated Si 2p and O 1s line shifts to lower binding energies as compared to pure SiO_2. The spectra bear strong similarities with those of wollastonite, "$CaSiO_3$". A comparable behavior was found for Mg-doped SiO_2 but not for K- or Cs-doped SiO_2, which show low activity in methanol formation.

Keywords: promoted Pd/SiO_2 catalysts, CO hydrogenation, methanol synthesis, promoter–support interaction, secondary ion mass spectrometry, X-ray photoelectron spectroscopy

1. Introduction

Conversion of synthesis gas to methanol is one of the large-scale industrial processes of heterogeneous catalysis. Catalysts applied in the low-pressure ICI process are based on $Cu/ZnO/Al_2O_3$. Also formulations with Pt group metals have been found active in oxygenate production. For example, promoted Pd/SiO_2 catalysts are highly selective in methanol formation [1–9], and represent interesting model systems, in particular for studying the mechanism and microkinetics of this reaction.

Initial studies of CO hydrogenation over supported Pd catalysts brought forth contradictory results: while Poutsma et al. [1] reported high selectivities towards methanol, Fajula et al. [7] found mainly methane formation. It seems clear by now that the main reason for this contradiction was the use of silica supports (Davison grade 57 versus grade 01) of different purity. In fact, Nonneman et al. [8], in a study with Rh catalysts, demonstrated Na and Fe contaminations in the commercial silica support to be responsible for the considerable activity towards ethanol. On the other hand, using pure SiO_2 at otherwise identical reaction conditions caused the disappearance of ethanol and the formation of hydrocarbons along with some actetaldehyde in the product spectrum. A recent study by Gotti and Prins [9] worked out the effect of Ca doping on Pd catalysts supported by pure silica. They found the selectivity to increase to > 99% methanol after doping with 1000 ppm. This increase was associated with a gain in activity by more than a factor of ten. Recent studies with La-doped catalysts led to further increases of the activity. On the other hand, methane formation appeared to be strongly suppressed meaning that CO dissociation is largely impeded on these promoted catalysts. Furthermore, as the authors found a clear correlation between the amount of Ca, the noble metal surface and the methanol activity, the hypothesis may be advanced that the formation of methanol occurs through formate intermediates on the support surface or in the interface between the support and the Pd particles. This scenario considers the Pd metal as the supplier for dissociative hydrogen which moves in a spillover process onto the support in order to subsequently react with formate to methanol.

There are a number of open questions as to the details of such a mechanism. For details see, e.g., ref. [9]. The present paper presents SIMS results (secondary ion mass spectrometry) performed in order to identify the relevant surface species occurring during methanol synthesis and to locate them either on the Pd metal or the support surface. Emphasis has been laid at demonstrating by means of XPS (X-ray photoelectron spectros-

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copy) a chemical interaction between the silica support and the promoter material.

2. Experimental

Catalysts were made by using standard preparation methods. Accordingly, ultra-pure SiO_2 obtained by hydrolysis of tetraethoxysilane (BET surface area 890 m^2/g) was impregnated (pore volume technique) with aqueous solutions of $Pd(NO_3)_2$ subsequently dried at 393 K for 16 h and calcined in air at 723 K for 2 h. Doping occurred by impregnating the catalyst precursor with the respective aqueous solutions of the promoter nitrate followed by drying at 393 K and calcination at 723 K for 2 h. All catalysts had palladium loadings of 5–6 wt% and a molar concentration of 5000 ppm of the promoter sufficient to cause saturated promoter action.

Silica samples free of Pd metal were impregnated by 10 wt% alkali (Li, Cs) and alkaline earth (Mg, Ca) nitrate solutions, dried and calcined under the same conditions as mentioned above. In order to avoid any possible effects resulting from slightly different support material compositions, silica from one batch was used for all samples.

The high-pressure reactor, attached to the UHV (ultra-high vacuum) surface analytical system was described in detail elsewhere [10]. In brief, the reactor works at a pressure up to 10 bar under flow conditions. Reactants and synthesis products are monitored on-line using a differentially pumped QMS (quadrupole mass spectrometer). The catalyst precursors were reduced at 623 K in a flow (10 sccm, whereby 1 sccm = 996 mbar $\ell\ s^{-1}$) of pure hydrogen at 1 bar for 90 min. In order to reach the activation temperatures heating ramps of 12 K/min were applied. After reduction the hydrogen was pumped off while the catalyst temperature was held at 623 K for 5 min.

The CO hydrogenation was carried out at a total pressure of 9 bar ($CO : H_2 = 0.5$) and at a reaction temperature of 553 K. Here the gas flow was 12 sccm. The reaction was quenched by slowly pumping off the syngas combined with a simultaneous decrease of the catalysts temperature.

Promoted Pd/SiO_2 catalysts were analysed for their surface composition by SIMS both after reduction and methanol synthesis. SiO_2 samples containing alkali and alkaline earth were subjected to an XPS analysis. A detailed description of the surface analytical setup can be found in ref. [11]. SIMS spectra were recorded using 2×10^{-8} mbar Ar ions with an energy of 5 keV. The ion source was operated with an emission current of 1 mA resulting in an ion beam intensity of approximately 10 nA/cm^2 (measured with a Faraday cup). To reduce the Ar ion current density impinging onto a surface unit of the catalyst the beam was scanned over an area of $2 \times 2\ mm^2$. Charge compensation of the otherwise nonconducting samples was achieved by making use of an electron flood gun ($E_{kin} = 5$–10 eV).

The XPS spectra were recorded using non-monochromatized Al Kα radiation ($h\nu = 1486.6$ eV). The X-ray source was operated at a power of 300 W (15 kV, 20 mA). The energy analyser was operated at a constant pass energy of 202 eV. The charge compensation of the samples was controlled by referencing to the Au $4f_{7/2}$ line of the sample holder as an internal standard [10] (Au $4f_{7/2} = 84.0$ eV).

3. Results and discussion

3.1. Catalytic studies

The influence of different types of promoter materials on the methanol formation rate is demonstrated in figure 1. As can be seen, lithium, calcium and lanthanum cause each a strong increase in the activity on heating to 553 K while passing CO/H_2 through the reactor. For comparison, pure SiO_2 remains catalytically inactive. We mention that Pd/SiO_2 showed a factor of about 50 lower activity in methanol production as promoted samples [9]. The relatively long time lags in both the onset of methanol detection and its steady state adjustment are due to the use of a capillary system for pressure reduction from 10 bar during reaction to the 10^{-6} mbar regime of the mass spectrometer. The characteristic mass signal of $m/e = 31$ for methanol was normalized to the $m/e = 28$ signal of CO to overcome small pressure fluctuations in the QMS chamber.

According to figure 1 the promoting effect towards methanol increases in the order Li < Ca < La. This finding is in good agreement with results obtained recently in studies with a large number of promoted catalysts at somewhat higher pressures (25 bar) but otherwise identical conditions of CO/H_2 ratios and temperatures [9,12]. A quantitative evaluation of the data was not performed. It will be shown that the mechanism of the reaction involves in a synergistic manner both the metal surface and the support so that the calculation of rates normalized to the metal surface area is not sensible.

3.2. SIMS analysis

Both promoted and unpromoted Pd/SiO_2 samples were subject of SIMS studies before and after CO hydrogenation. Employing static conditions with negligible sputter damage ensured that one and the same sample showed identical kinetic behavior in the catalytic reactor even after several cycles of SIMS analysis and CO/H_2 runs.

The results of a La-doped Pd/SiO_2 surface analysis are depicted in figure 2. Absolute count rates have been normalized to the most intensive peak, $m/e = 28$. For the sake of clarity, difference spectra have been calcu-

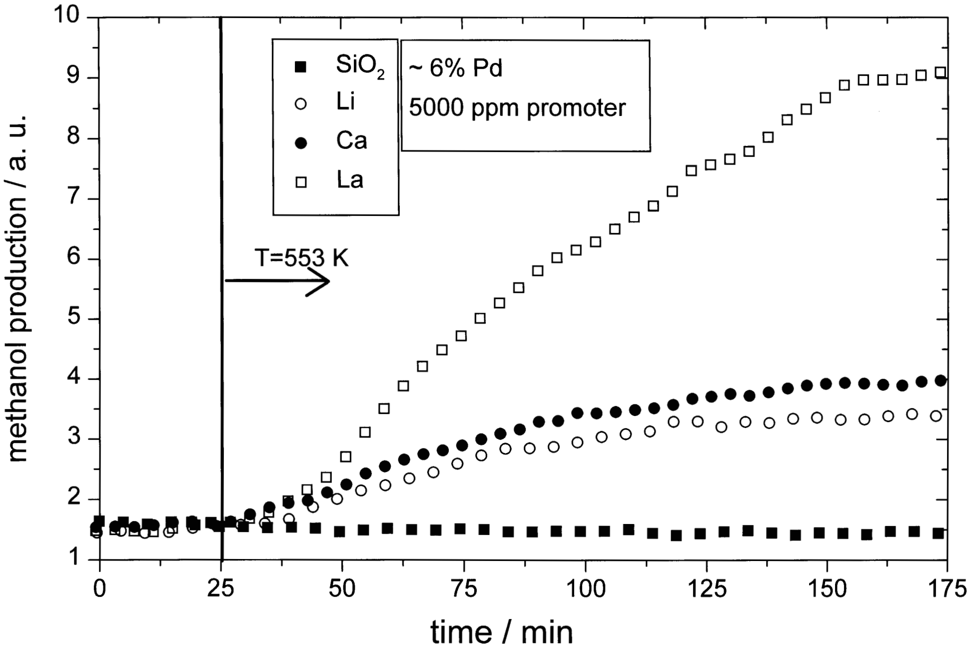

Figure 1. Methanol formation followed by mass spectrometry (31 : 28 amu) for four different samples. After reaching the reaction temperature of 553 K methanol is formed on promoted Pd catalysts, whereas no detectable methanol signal is observed for pure SiO_2.

lated (bottom part of figure 2) from the normalized spectra. Such a procedure may lead to spectral features with negative count rates due to the occurrence of differences in signal shapes and intensities. These parts of the spectra have been removed from figure 2 provided the difference in integrated peak areas between positive and negative lobes was less than a few percent only.

Figure 2 contains the mass range up to $m/e = 100$. Various types of ions are visible which can be directly related to parent or fragmented species adsorbed on the catalyst surface. As to be expected, there are large amounts of hydrogen remaining at the sample surface after stopping the synthesis reaction. $m/e = 28$ is absent because of the count rate normalization procedure. The catalytic formation of methanol is indicated by the occurrence of adsorbed methoxy which can be

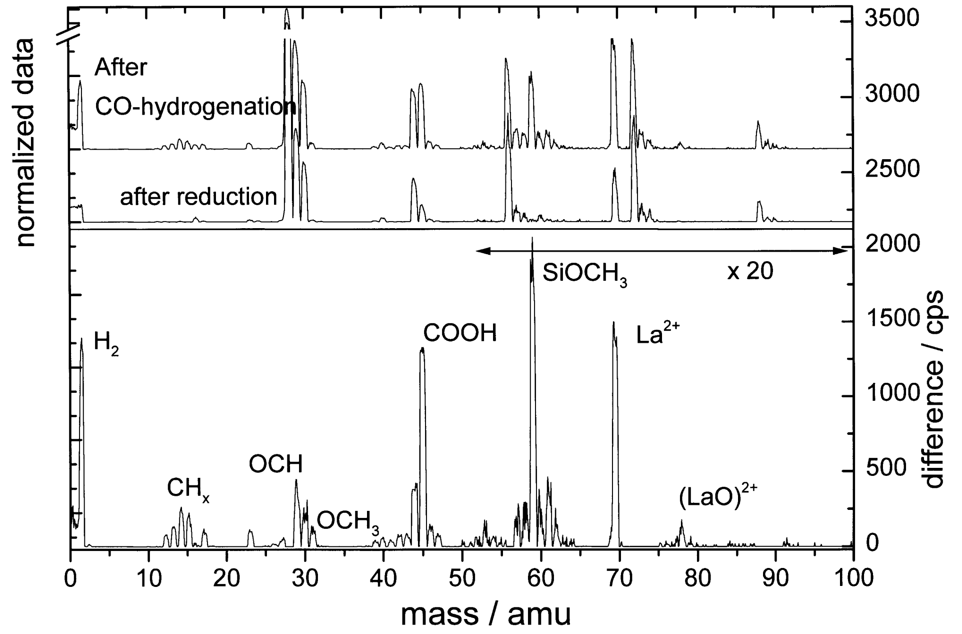

Figure 2. Normalized SIMS data for a Pd/SiO_2 catalyst doped with 5000 ppm La. Top: data recorded after reduction and after CO hydrogenation. Bottom: difference spectrum.

regarded as its immediate precursor species. Besides $m/e = 31$ there is clear indication for a peak at $m/e = 59$. We conclude that OCH_3 groups are bound to Si atoms of the silica support. We mention that some methoxy has also been found to be bound to La atoms, but the respective Pd-related species were only observed in very small or even negligible amounts. Within this scenario, OCH_x^+ species result most likely from the sputter-induced fragmentation of methoxy either bound to Si or La. This, however, does not necessarily mean that the formation of methoxy species on Pd metal is entirely excluded. In previous SIMS studies of methanol interaction with Pd (111) single crystals, Rebholz and Kruse [11] demonstrated the strong dependence of $PdOCH_3^+$ ion intensities on the temperature. Unless methanol was continuously dosed to the sample the respective cluster peaks were negligible at 300 K. Methanol adsorption experiments with promoted Pd/SiO_2 catalysts did not result in significant $PdOCH_x^+$ detection even under continuous gas supply. On the other hand, a $PdCH_3^+$ species was detected in these experiments indicating O–C bond breaking in methanol adsorbing on Pd particles. This reaction route has also been identified in single-crystal work [11,13].

Besides the parent methoxy, typical ionic fragments are present in the mass spectra as well. For example, CH_x^+ species occur with fairly large intensity in figure 2 as they did in studies with (111) oriented Pd single crystals [11]. $PdCH_x^+$ species would have been expected to appear if significant amounts of methane were formed during CO hydrogenation over Pd metal. This, however, seems not to be the case and is in line with the finding that La-promoted Pd/SiO_2 catalysts produce methanol with more than 99% selectivity. Signals in the range $m/e = 40$–43 are assigned to $SiCH_x^+$. Their intensities are similar to those of CH_x^+. We mention here that $SiCH_3^+$ species have also been found in considerable amounts in experiments where methanol was continuously dosed to the catalyst surface.

Besides reactant and product precursor species of the methanol synthesis a number of further species are observed which need further inspection. For example, the signals at $m/e = 44$ and 45 indicate the formation of formate. The deconvolution of $COO(H)^+$ and $SiO(H)^+$, which both contribute to the observed mass peaks, has been achieved by a careful analysis of the Si isotope distribution. In order to be sure, this analysis has been performed with a large number of spectra obtained with different samples of the same chemical composition after running the CO hydrogenation at similar or identical reaction conditions.

Methanol adsorption on the catalyst surface also led to an increased intensity in the $m/e = 45$ cluster intensity while the OH^+ cluster at $m/e = 17$ remained constant. If the increased signal of $m/e = 45$ were due to a $SiOH^+$ species the $m/e = 17$ signal should have increased too. Thus the $m/e = 45$ signal is due to a formate which is formed upon methanol adsorption at the catalyst.

The SIMS results obtained for Li- or Mg-promoted catalysts are similar to those presented here for the La case. Neither COO(H) nor $SiOCH_3$ species have been observed for pure or promoted SiO_2 samples.

Putting into more general perspective the SIMS results presented in this paper, it seems that a reaction mechanism is in operation which is best described in terms of a synergy between the Pd metal and the support surface. Accordingly, the main task of the noble metal is to activate hydrogen and to supply it in atomic form to the support for further reaction. The absence of OCH_x species on the Pd particle surface both after synthesis and while continuously dosing the catalyst with methanol at low pressures indicates that the immediate precursor stages of the synthesis product, methanol, are located on the support surface. Both formate and Si-bonded methoxy have been clearly identified by SIMS. This is in accordance with infrared results obtained by various authors in studies with promoted catalysts [4,14–16].

The question for active site formation in the interface between the metal particle and the support has been formerly addressed by means of XPS. While Hicks et al. [17] were unable to show metal–support interactions between palladium and silica, Pitchon et al. [18] found a binding energy of the Pd $3d_{5/2}$ line in alkali-promoted Pd/SiO_2 which was lower than in promoter-free catalysts. Such local interactions are not accessible by the SIMS method. On the other hand, as has been shown in this paper, the SIMS analysis of ionic cluster compounds and their fragments provides insight into the nature of the relevant chemical species occurring on either the support, promoter or metal surface. This information cannot be easily gleaned from XPS. This latter method allows, however, to study chemical phase transformations or specific interactions leading to structural changes of the catalytically active phase, for example, by an analysis of chemical states of atoms.

3.3. XPS analysis

This section is aimed at providing evidence that the silica support undergoes strong interactions with the promoter material rather than simply providing favourable sites for an anchoring of promoter atoms as, for example, in the interface to Pd particles. Due to the limited detection sensitivity of the XPS method we used silica samples which were doped with relatively large amounts, 10 wt% (referenced to the respective oxide). In order to put into more general perspective the action of various promoters we present here the results for calcium-, magnesium-, potassium- and cesium-containing samples. Lanthanum-doped samples were examined with XPS too, but due to the low cross section for Auger transitions we were not able to determine the Auger parameter ($\alpha = E_{\mathrm{kin}}(\mathrm{Auger}) + E_{\mathrm{B}}(\mathrm{photoemission})$) and we therefore do not present the results here. The XP-spectra were recorded directly after activation, i.e. after passing hydrogen through the samples following the same procedure as for Pd-containing catalysts. Pure silica and wollastonite (Ca-silicate, $CaSiO_3$, with sheet structure) were used as reference substances.

Figure 3 shows the results obtained for the Si 2p and O 1s energy regions. We estimate the absolute error in the position of these lines to be ±0.2 eV. This estimation takes into account the amorphous peak broadening and the charge correction of the insulating samples; no shift of the lines was observed during data acquisition. The values of $E_{\mathrm{B}} = 103.3$ eV for Si 2p and $E_{\mathrm{B}} = 532.6$ for O 1s photoemission from SiO_2 are in accordance with literature data and so are the values of 102.2 and 531.4 eV for the respective lines in wollastonite [19,20]. As can be seen in figure 3, the O 1s and Si 2p peak positions are at a lower energy than those of the pure SiO_2 sample. While the values for the K- and Cs-doped samples are still very close to those for silica, the Ca- and Mg-doped samples exhibit a significant downward shift by about 0.8 eV for the O 1s line and 0.5 eV for the Si 2p line. Following arguments developed by Barr [21], the formation of a mixed oxide $A_jO_kB_l$ from different oxides A_xA_y and B_mO_n is associated with a shift in the binding energy of respective lines such that the peak positions lie in-between those of the source materials (whereby parameters like the electronegativity and the radius of the cations can influence the extent to which the shift occurs). Wollastonite is a good example for this interaction. The Si 2p binding energy is significantly lowered as compared to pure silica and the O 1s binding energy lies between the value for pure silica and the one for metal oxides (CaO: $E_{\mathrm{B}} = 531.0$ eV, MgO: $E_{\mathrm{B}} = 531.3$ eV [22]). Accordingly, the strong shifts of Si 2p and O 1s lines of Ca-doped samples lead us to conclude that the silica has been largely transformed into a wollastonite-like material during the hydrogen treatment at 623 K. A similar behavior is observed for Mg-doped samples (for example, Barr et al. found values of Si 2p = 102.5 eV and O 1s = 531.6 eV for Crysotile ($Mg_3Si_2O_5$) [23])). By contrast, the slight or even negligible line shifts of K- and Cs-doped samples indicate weak interactions between these atoms and the SiO_2 matrix.

The above conclusions are confirmed by an analysis

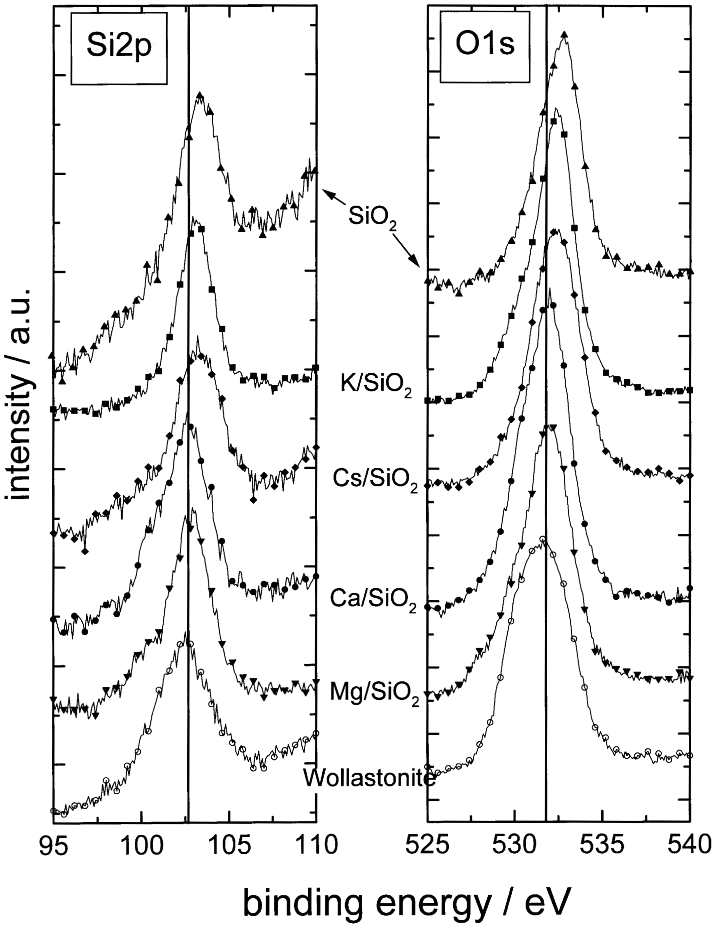

Figure 3. XP-spectra of the Si 2p and O 1s region for different promoter/silica samples; pure silica and wollastonite as reference substances; measurements after reduction treatment in H_2 of the samples. Charge compensation by placing the Au $4f_{7/2}$ line at 84.0 eV.

of the Auger parameters for the respective cations, which are summarized in table 1. The usefulness of calculating α values has been demonstrated for a large number of chemical compounds (note that α is much more sensitive to changes in the chemical environment than are photoemission lines; this is because the emission of an Auger electron leaves a twofold ionised atomic system so that relaxation effects become more important). Most importantly, the Auger parameter is by definition independent of the sample charging. For comparison, the difference between α values determined from our data and from respective oxides (CaO, MgO, KOH) are given in the same table 1. As can be seen, the α value for Ca is exactly the same as for wollastonite and the $\Delta\alpha$ values of Ca/SiO_2 and wollastonite are very close. Unfortunately, few data about "SiOMg" compounds exist in the literature. Seyama and Sonoma [24] examined talc ($Mg_3Si_4O_{10}$) and found an α(Mg) value of 2484.4 eV which is by about 1 eV higher than ours (this is not too surprising because it seems unlikely that our silica sample suffers a transformation into just talc). No literature data could be found for more "simple" Mg-silicates like forsterite (Mg_2SiO_4), enstatite ($Mg_2Si_2O_6$) or crysotile ($Mg_3Si_2O_5$). However, the α(Mg) value for Mg/SiO_2 follows the same *trend* as the α(Ca) value for Ca/SiO_2, i.e. it is significantly lower than for the corresponding oxide. Quite differently from Mg- and Ca-containing samples, the α values of K and Cs are close to those of KOH and CsOH, respectively.

The results presented above suggest that Ca- and Mg-doped samples may cause a chemical/structural transformation of the silica matrix at the rather low temperature (623 K) of the hydrogen treatment. This is surprising in view of the 1800 K usually applied to form synthetic wollastonite from SiO_2 and CaO [25]. Whether, in the case of Ca/SiO_2, a wollastonite-like structure is really formed, must await further studies. Though the doping levels with Ca- or Pd-based catalysts are usually lower than 10 wt% as used here, it seems reasonable to assume that *local* structural changes in the silica matrix take place as well and influence the catalytic activity during CO hydrogenation.

Table 1

XPS peak positions for different promoter/silica samples and the two reference substances SiO_2 and wollastonite. In the two leftmost columns the values for the Si 2p and O 1s lines are shown. The metal Auger parameter for the respective metal is given is column 3. (The following lines were used to determine the Auger parameter: Ca: $2p_{3/2}$, $L_2M_{23}M_{23}$ / Mg: 1s, $KL_{23}L_{23}$ / K: $2p_{3/2}$, $L_3M_{23}M_{23}$ / Cs: $3d_{5/2}$, $M_4N_{45}N_{45}$). The differences between the measured Auger parameters and the Auger parameters of the respective metal oxides are listed in column 4

Sample	Si 2p (eV)	O 1s (eV)	α-ME (eV)	$\Delta\alpha$ (eV)
SiO_2	103.3 ± 0.2	532.5 ± 0.1	–	–
wollastonite	102.3 ± 0.1	531.6 ± 0.1	638.5	1
Ca/SiO_2	102.7 ± 0.1	531.8 ± 0.1	638.6 ± 0.1	0.9
Mg/SiO_2	102.7 ± 0.1	531.8 ± 0.1	2483.5 ± 0.3	1.7
K/SiO_2	103.1 ± 0.1	532.4 ± 0.2	543.6 ± 0.3	0.2
Cs/SiO_2	103.1 ± 0.1	532.2 ± 0.2	1292 ± 0.2	0.3

The idea of giving the silica support an active role in the CO hydrogenation has also been developed in previous research by others. Using $C^{18}O$ in the CO hydrogenation on alkali- and alkaline earth-promoted Pd catalysts, Kikuzono et al. [4] found ^{16}O-containing oxygenate products and suggested an oxygen exchange with the support via a formate intermediate. Pitchon et al. [26] found a correlation between the methanol activity and the number of free hydroxyl groups on silica using a Li-promoted Pd/SiO_2 catalyst. A change in the local structure of the silica by chemical interaction with the promoter was not reported in these studies.

4. Summary

In the present investigation the CO hydrogenation over promoted Pd/SiO_2 catalysts was studied in a high-pressure reactor attached to a UHV chamber with facilities for SIMS and XPS. Catalysts subject to CO hydrogenation were subsequently studied by SIMS. The promoter–support interaction was investigated by means of XPS.

The activity of promoted samples increased in the order $Li < Ca < La$. SIMS studies revealed the existence of methoxy bound to the silica ($SiOCH_3$) as well as to the promoter (Ca, La). Formate was identified in relatively high amounts by the same method. No such species were found on the Pd particle surface. The amount of PdO compounds in the SIMS spectra was found to be statistically insignificant for both promoted and unpromoted samples. Methanol adsorption experiments under continuous gas supply yielded corroborating evidence that species supposed to act as intermediates of methanol synthesis/decomposition are not adsorbed on Pd metal, contrary to single-crystal work.

The findings suggest a reaction mechanism with a synergy effect between the support and the Pd metal. The main task of the noble metal is to act as a supplier of atomic hydrogen which is then spilled over to the support, where the subsequent hydrogenation takes place.

In order to demonstrate a promoter–support chemical interaction, XPS studies were performed in the absence of Pd metal. For Ca and Mg the Si 2p and O 1s binding energies shift to lower values if compared to the positions for pure silica and the respective metal Auger parameter deviates significantly from the values of the respective metal oxide. The shifts can be interpreted in terms of the formation of a mixed oxide at the surface, e.g. a silicate. No such shifts were observed with Cs- or K-containing silica. These findings correlates with a high/low methanol activity in CO hydrogenation over alkali/alkaline earth-promoted Pd/SiO_2 catalysts.

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