Effect of Ca loading and SiO$_2$ type on Pd for CO hydrogenation to methanol

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ABSTRACT

The influence of Ca promotion of 2 wt % of Pd/SiO$_2$ on CO hydrogenation to methanol was studied using different levels of Ca loading (up to 2 wt % of Ca) and two different SiO$_2$ supports (Davisil grades 634 and 644). Ca was found to have a selective promoting effect on Pd for CO hydrogenation towards methanol. The highest increase in the avergae site activity for methanol formation (TOF$_{CH3OH}$) was found to be at low-to-moderate Ca loading levels (0.4 to 0.7 wt%), which was related to the direct involvement of the promoter in methanol synthesis. However, having Ca loading higher than 0.7 wt % resulted in the decrease of the activity of the Pd catalyst probably due to the partial blockage of the active surface of the catalyst by the promoter. The type of the SiO$_2$ support, on the other hand, was found to have some impact on the activity of Pd for CO hydrogenation. This was attributed to differences in the levels of metallic impurities present (Na, Mg and Ca) with possible promoting effects (SiO$_2$ grade 644 had higher concentrations of these impurities than grade 634).

Key Words: Ca; CO hydrogenation; methanol; Pd/SiO$_2$

INTRODUCTION

It is well established that Pd has a weak ability to discociate CO and a moderate ability to activate H$_2$, thus, it is considered to be one of the best active metals for the synthesis of methanol from the reaction of CO and H$_2$ (Poutsma *et al*. 1978, Ryndin *et al*. 1981). The activity and the selectivity of supported Pd catalysts for CO hydrogenation can be altered by the addition of promoters. Li, Na, Mg, Ca and La have been found to have a significant promoting effect on the activity of supported Pd catalysts for methanol synthesis (Kikuzono *et al*. 1981, Driessen *et al*. 1983, Deligianni *et al*. 1985, Kelly *et al*. 1986, Hahm & Lee 1990, Kazi *et al*. 1995, Gotti & Prins 1996, 1998). The increase in the rate of methanol formation of Pd catalysts due to the addition of promoters, such as the ones mentioned above, can be a function of many of factors such as the type of the precursors used and the method of preparation.

Ca has been found to be one of the best promoters for Pd and other similar metals such as Pt for the synthesis of methanol (Kelly *et al*. 1986, Hahm & Lee 1990, Gotti & Prins 1998, Watling *et al*. 1999). Ca was found to be a much better promoter than La for methanol synthesis over Pd (Hahm & Lee 1990); however, the results of another study (Gotti & Prins 1998) show that among the many different promoters studied La was found to be the best promoter followed by Ca. In addition, by comparing the results of these two cited studies (Hahm & Lee 1990, Gotti & Prins 1998), it can be noticed that the relative increase in the rate of formation of methanol due to Ca addition (for the same Ca to Pd loading and the same reaction conditions) was not the same in both cases. Thus, even though some aspects of the promotion of supported Pd catalysts by Ca for methanol synthesis have been studied, it is rather a complicated subject and must be further investigated in order to better understnad this promotion. The purpose of this study was to investigate the impact of Ca promotion of supported Pd for CO hydrogenation in terms of two main aspects: varying Ca loading and type of SiO_2 support.

EXPERIMENTAL

Materials

The two different silica supports used were Davisil grade 634 and Davisil grade 644. The surface areas, pore volumes and mesh sizes were as follows: SiO_2 type Davisil grade 634; 480 m^2/g, 0.75 cm^3/g and 100 - 200 mesh; SiO_2 type Davisil grade 644; 300m^2/g, 1.15 cm^3/g and 100-200 mesh, respectively. The palladium precursor used to prepare the catalyst was $PdCl_2$ (Aldrich-catalog number 28,360-6). The calcium precursor used to promote the Pd catalysts was $CaCl_2.2H_2O$ (Aldrich-catalog number 47,087-2).

Elemental analysis

Incluctive Coupled Plasma Spectroscopy (ICP) was used to determine the impurities of the two types of SiO_2 used. Fisons Instrument model 3410 ICP was used for this purpose because of its high accuracy. The supports were scanned for various metallic impurities.

Catalyst nomenclature

Each one of the two base catalysts prepared is designated by three letters followed by a number. The first two letters are Pd, which refer to the active metal used in preparing all the catalysts used in this investigation. The third

letter is S, which refers to the support used, which is SiO$_2$. A number follows the third letter, either 1 or 2, which refers to the type of the support used (1 for SiO$_2$ type Davisil grade 634 and 2 for SiO$_2$ type Davisil grade 644). Thus, the base catalysts prepared are named Pd/S1 and Pd/S2. The Ca-promoted Pd catalysts are designated by a number reflecting the weight percentage of Ca and then its symbol (Ca), followed by either symbols: Pd/S1 or Pd/S2.

Catalyst preparation

Two batches of base catalyst each having 2 wt% of Pd on SiO$_2$ were prepared by the incipient wetness technique using an aqueous solution of PdCl$_2$. The first batch was prepared using SiO$_2$ type Davisil grade 634 and the second using the other grade of SiO$_2$. For the first batch of base catalyst almost 0.75 cm^3 of liquid was used per gram of SiO$_2$ type Davisil grade 634, while for the other batch almost 1.15 cm^3 of liquid was used per gram of SiO$_2$ type Davisil grade 644. After the impregnation step, the two base catalyst batches were dried in an oven overnight at 115°C. The dried catalysts were then calcined in flowing ultra high pure air (99.999% pure) by raising the catalyst temperatures to 400°C with a heating rate of 2°C/min and holding for 5 hours.

The Ca-promoted Pd/SiO$_2$ catalysts were prepared by loading the base catalysts with aqueous solutions of CaCl$_2$ using the incipient wetness technique. After this impregnation step, the catalysts were dried in an oven at 115°C. The dried Ca-promoted Pd/SiO$_2$ catalysts were then calcined in flowing ultra high pure air (99.999% pure) by raising the catalyst temperature to 400°C with a heating rate of 2°C/min and holding for 5hrs. Each base catalyst (either Pd/S1 or Pd/S2) was loaded with different amounts of Ca (0.4, 0.7, 1.0 and 2.0 wt% of Ca).

CO Chemisorption

CO chemisorption measurements were carried out using a Micromeritics ASAP 2010 sorptometer. A Pd catalyst (0.250 gram) was loaded in a glass tube and was reduced by ultra high pure H$_2$ (99.999%) by varying the temperature to 400°C with a heating rate of 1°C/min and holding for 2 hours. Desorption of hydrogen from the catalyst surface was done at 400°C for 30 minutes, followed by cooling the sample to room temperature. CO was then introduced to the evacuated cell containing the reduced catalyst at room temperature. Total adsorption data were collected by exposing the catalyst to the adsorptive gas (CO) at a series of precisely controlled pressures ranging between 200 and 400 mm Hg. The total amount of chemisorbed CO molecules (CO$_{total}$) was calculated by extrapolating the total adsorption isotherm to zero pressure. After

the determination of the total adsorption isotherm, the chemisorption cell was evacuated, and the reversible adsorption isotherm was measured. This isotherm was also extrapolated to zero pressure to obtain the reversible amount of chemisorbed CO molecules ($CO_{reversible}$).

Carbon monoxide hydrogentation

A fixed-bed reactor was used for studying the CO hydrogenation reaction, and differential reaction conditions were employed to minimize mass and heat transfer limitations. A flow of 100 cc/min of ultra high pure H_2 (99.999%) was used first to reduce 0.150 gram of a catalyst by ramping the temperature 2°C/min to 400°C and holding for 5 hours. After completing the reduction, the reaction was started at 220°C and 1 atm by setting the flow of the ultra pure H_2 and CO to be 100 and 20 cc/min, respectively. After 5 minutes of reaction, the first sample of the products was taken and analyzed using a gas chromatograph (GC) equipped with a 6 ft Porapack-Q column and an FID detector. The CO hydrogenation reaction was followed for 24 hours, where a steady-state condition was assumed.

The dependency of the rate of methanol formation on the partial pressures of H_2 and CO was studied at steady-state. This dependency was investigated for Pd/S1 and 0.7Ca/Pd/S1 catalysts. For this purpose, the total flow rate of the reactants was kept constant (120 cc/min), and it was achieved by the addition of an inert make up gas (He), whenever needed. The H_2 flow rate was varied between 40 and 100 cc/min, while that for CO was varied between 10 and 40 cc/min, with He providing the balance.

RESULTS

Elemental analysis

Table 1 shows the results of the inductive coupled plasma spectroscopy analysis for the impurities in the supports used in this investigation. Both supports (SiO_2 type Davisil grades 634 and 644) contained the following impurities: Na, Mg, Ca and Fe. The concentration of Fe in the two supports was almost the same. However, the concentrations of Mg and Ca in SiO_2 type Davisil grade 644 were almost twice their concentrations in the other support. In addition, Na concentration in SiO_2 type Davisil grade 644 was roughly three times its concentration in the other type of SiO_2.

Table 1: Supports impurities

Support	Impurity	Concentration[a] (ppm)
SiO$_2$ type Davisil grade 634	Na	170
	Mg	53
	Ca	189
	Fe	36
SiO$_2$ type Davisil grade 644	Na	558
	Mg	100
	Ca	366
	Fe	39

* From ICP. Maximum error $= \pm 3\ \%$.

Catalyst characterization

The total and reversible chemisorbed CO for the unpromoted and Ca promoted Pd catalysts are reported in Table 2. It can be noticed that for the same Ca loading (ranging between 0 and 2 wt%) the catatlyst prepared using SiO$_2$ type Davisil grade 634 had higher total and reversible amounts of chemisorbed CO than the ones using the other grade of SiO$_2$. The irreversible CO uptake (CO$_{irreversible}$ = CO$_{total}$ - CO$_{reversible}$) relative to the amount of Pd present for each catalyst ranged between 0.21 and 0.35 for the Ca/Pd/S1 catalysts, while for the Ca/Pd/S2 catalysts it ranged between 0.10 and 0.20.

Table 2: Characteristics of the catalysts

Catalyst	Total chemisorbed CO[a] (μmol/g cat)	Reversible chemisorbed CO[a] (μmol/g cat)	CO$_{irreversible}$/Pd
Pd/S1	83	19	0.34
0.4Ca/Pd/S1	81	16	0.35
0.7Ca/Pd/S1	57	12	0.24
1.0Ca/Pd/S1	50	11	0.21
2.0Ca/Pd/S1	86	23	0.34
Pd/S2	40	8	0.17
0.4Ca/Pd/S2	24	5	0.10
0.7Ca/Pd/S2	38	8	0.16
1.0Ca/Pd/S2	42	9	0.18
2.0Ca/Pd/S2	52	14	0.20

* Maximum error $= \pm 5\%$.

Table 3: Steady-state results of CO hydrogenation[a]

Catalyst	% CO conversion	% Methane selectivity	% Ethane selectivity	% Methanol selectivity	Total rate of CO conversion (μmol/g cat/s)	Rate of CH$_3$OH (μmol/g cat/s)	TOF$_{CH3OH}$[b] (10^{-3} S^{-1})
Pd/S1	0.21	29	9	62	0.19	0.12	1.8
0.4Ca/Pd/S1	0.24	25	9	66	0.22	0.14	2.2
0.7Ca/Pd/S1	0.30	23	9	68	0.27	0.19	4.1
1.0Ca/Pd/S1	0.24	23	9	68	0.22	0.15	3.8
2.0Ca/Pd/S1	0.23	27	11	62	0.21	0.13	2.1
Pd/S2	0.22	37	14	49	0.20	0.10	3.1
0.4Ca/Pd/S2	0.24	36	14	50	0.22	0.11	5.8
0.7Ca/Pd/S2	0.24	18	8	74	0.22	0.16	5.4
1.0Ca/Pd/S2	0.20	20	8	72	0.18	0.13	3.9
2.0Ca/Pd/S2	0.18	22	10	68	0.16	0.11	2.9

[a] Reaction conditions: 220°C, 1 atm and H$_2$/CO = 5.
[b] TOF$_{CH3OH}$ calculated by dividing the rate of CH$_3$OH formation by CO$_{irreversible}$.

CO hydrogenation

Table 3 shows the results of CO hydrogentation for all the Pd catalysts at steady-state for H$_2$ to CO ratio of 5 to 1, and at a temperature and a pressure of 220°C and 1 atm, respectively. The steady-state results of the CO hydrogenation reaction were taken after 24 hours of reaction. The highest CO conversion under the conditions used was equal to 0.3%, which meant that differential reaction conditions could be assumed. Thus, both mass and heat transfer limitations had no effect on the rates of reactions that were obtained. In addition, the highest CO conversion to methanol was much less than the equilibrium conversion of CO to methanol under the conditions applied. It has to be mentioned that blank runs with SiO$_2$ only did not show any detectable activity for CO hydrogenation for both supports used in this investigation.

From the results in Table 3 it can be noticed that for the first series of Pd catalysts (the Ca/Pd/S1 catalysts) the total rates of CO conversion of the Ca-promoted catalysts were higher than that for the unpromoted catalyst for all the different Ca loading levels used. However, for this catalyst series the total rate of CO conversion increased as the Ca content increased up to a weight percentage of 0.7% then decreased as the loading of Ca increased further. The promoted Pd/SiO$_2$ with the highest Ca content, 2.0 Ca/Pd/S1, was slightly more active than the base catalyst, Pd/S1. For the second series of Pd catalysts (the Ca/Pd/S2 catalysts), on the other hand, the total rate of this reaction for Pd catalysts containing Ca loading levels of 0.4 and 0.7 wt % was higher than that for the
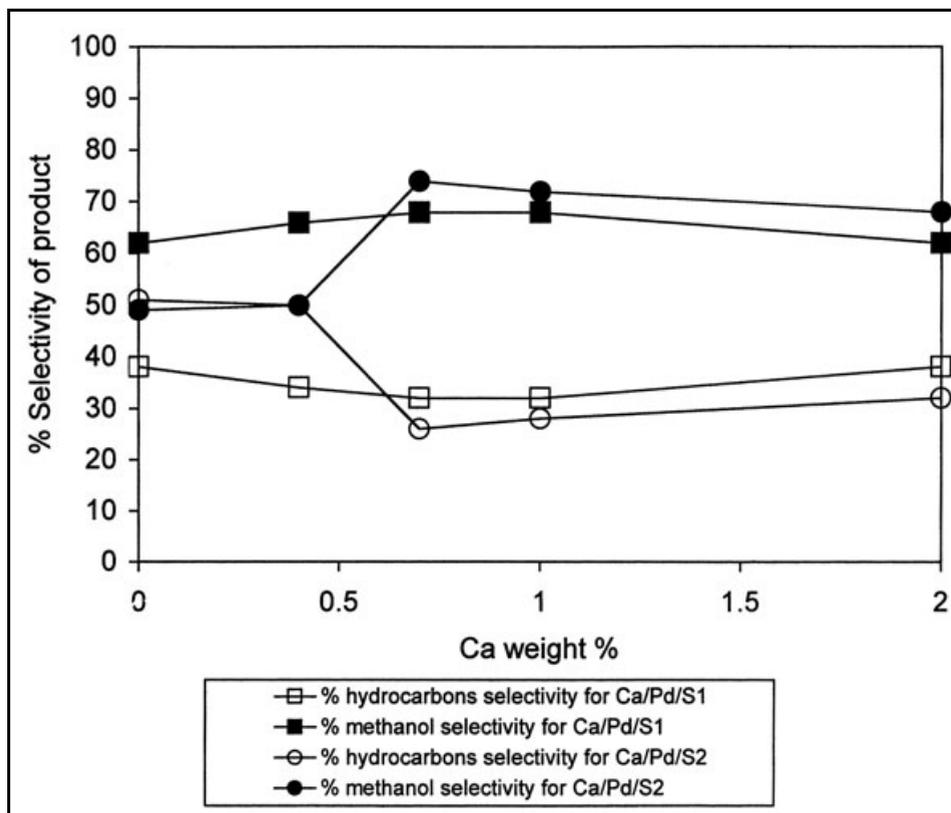
Fig. 1. Product selectivity at steady-state as a function of Ca loading.

base catalyst, Pd/S1, Table 3. Nevertheless, by increasing the Ca content of the Pd catalysts more than 0.7 wt%, the overall rate of CO hydrogenation decreased to lower values than for the base catalyst, Pd/S2.

The product selectivities are reported in Table 3 at steady-state for Ca/Pd/S1 and Ca/Pd/S2 catalysts as a function of Ca content. For the Ca/Pd/S2 catalysts, varying Ca loading had more impact on the product selectivities than for the other catalyst series. This was clearly shown in Fig. 1, where the selectivities of hydrocarbons (methane and ethane) and of methanol were plotted against Ca loading for the two catalyst series. For the Ca/Pd/S1 catalyst series, methanol selectivity varied between 62 and 68% upon Ca doping, while methane and ethane selectivities were in the range of 23 to 29%, and 9 to 11%, respectively. On the other hand, for the Ca/Pd/S2 catalyst series, methanol selectivity increased from 49% for the base catalyst, to as high as 74% for the 0.7Ca/Pd/S2 catalyst. In addition, methane and ethane selectivities were the highest for the unpromoted catalyst, Pd/S2, 37 and 14%, respectively, and decreased to as low as 18 and 8%, respectively, due to Ca promotion.
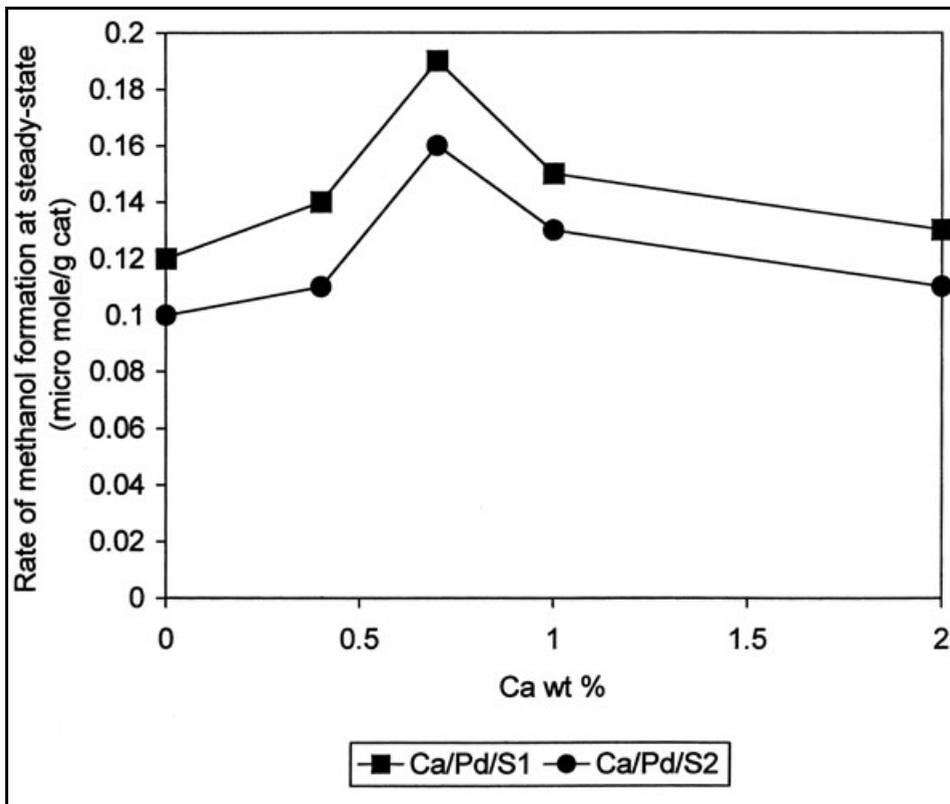
Fig. 2. Rate of methanol synthesis at steady-state for Ca/Pd/S1 and Ca/Pd/S2 catalysts
as a function of Ca loading.

The promoted catalysts had higher steady-state rates of formation of methanol than the unpromoted catalysts for both catalyst series (Fig. 2). The steady-state rates of formation of methanol for the Ca/Pd/S1 and Ca/Pd/S2 catalysts had maximum values at Ca loading of 0.7 wt %. For both catalyst series having Ca loading of 2.0 wt % resulted in near the disappearance of the positive impact of Ca doping on the rate of CH_3OH formation.

Table 3 shows that the TOF_{CH3OH} (average site activity for CH_3OH formation was calculated by dividing the rate of CH_3OH formation at steady-state by the irreversible CO uptake) for the Ca/Pd/S1 and Ca/Pd/S2 catalysts was changed upon Ca loading. It is clear that for Ca/Pd/S1 catalysts, increasing the Ca content to 0.7 wt% resulted in doubling the TOF_{CH3OH} value relative to the base catalyst, Pd/S1. But, increasing the Ca loading more than 0.7 wt % resulted in the disappearance of the positive impact of Ca doping on the value of TOF_{CH3OH}, particularly at 2.0 wt % of Ca. For the Ca/Pd/S2 catalysts on the other hand, loading the Pd catalyst by 0.4 wt % of Ca was enough to almost double the TOF_{CH3OH}. However, by increasing the Ca content more than 0.4
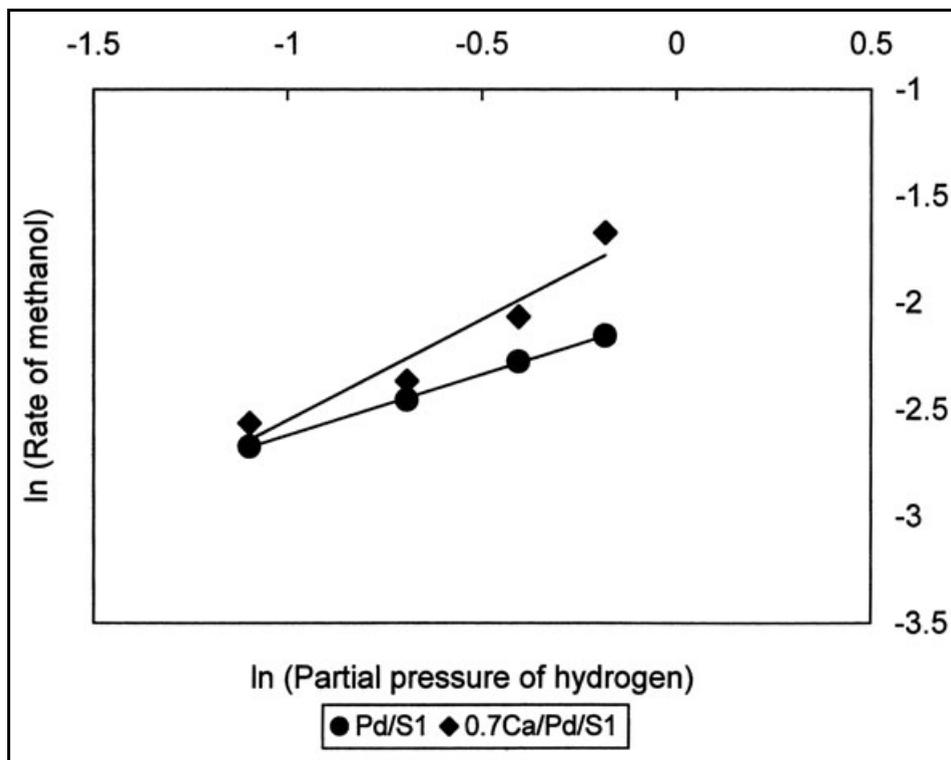
Fig. 3. The dependence of the rate of formation of methanol on the partial pressure of hydrogen for Pd/S1 and 0.7Ca/Pd/S1 catalysts.

wt% for the Ca/Pd/S2 catalyst series, the TOF$_{CH3OH}$ decreased and the TOF$_{CH3OH}$ of the 2.0 Ca/Pd/S2 catalyst was even less than that for the base catalyst, Pd/S2. For any Ca loading used, the TOF$_{CH3OH}$ was higher for the Ca/Pd/S2 catalysts than for the Ca/Pd/S1 catalysts.

The power law expressions for the rate of formation of methanol were found for Pd/S1 and 0.7Ca/Pd/S1 catalysts at steady-state. This was achieved by means of plotting in a log-log mode the rate of methanol formation versus the partial pressure of H$_2$ at a constant partial pressure of CO (Fig. 3) and versus the partial pressure of CO at a constnat partial pressure of H$_2$ (Fig. 4). The following expressions were found for the rate of formation of methanol:

For unpromoted Pd/S1 catlyst:

$$\text{Rate}_{\text{methanol}} = k_1 \ P_{H2}^{+0.57} \ P_{CO}^{+0.34} \tag{1}$$

For 0.7Ca/Pd/S1 catalyst:

$$\text{Rate}_{\text{methanol}} = k_1' \ P_{H2}^{+0.94} \ P_{CO}^{+0.29} \tag{2}$$
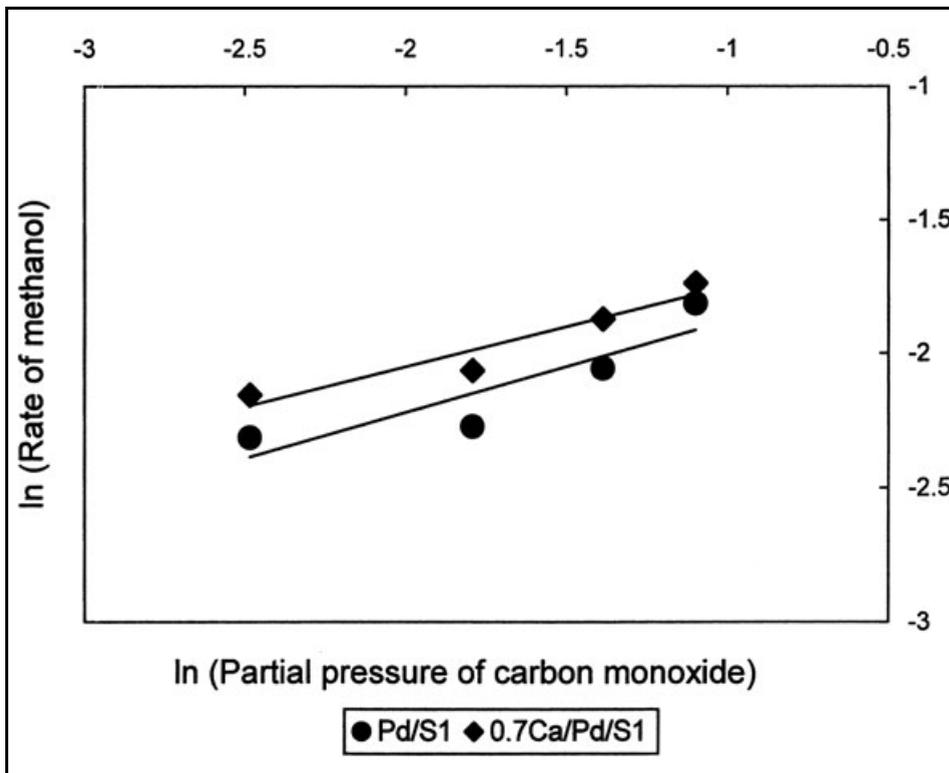
Fig. 4. The dependence of the rate of formation of methanol on the partial pressure of carbon monoxide for Pd/S1 ad 0.7Ca/Pd/S1 catalysts.

DISCUSSION

Impact of varying Ca loading

In order to focus on the effect of the Ca content on the catalytic properties of the Pd catalyst prepared, catalysts will be compared having the same support. For each catalyst series, the CO uptake decreased as the Ca loading increased to a certain content, then the CO uptake increased for higher Ca loadings to values almost equal or even slightly higher than those for the base catalysts (Table 2). Increasing Ca loading up to a Ca/Pd atomic ratio of 0.33 (Gotti & Prins 1998) resulted in the decrease of the irreversible amount of chemisorbed H_2. Over this range of Ca loading they found that Ca-promoted Pd/SiO$_2$ catalysts had higher activity for CO hydrogenation towards methanol synthesis than the Pd/SiO$_2$ base catalyst due to the development of a Ca-Pd active interface (Gotti & Prins 1998). Studies of Pd/SiO$_2$ catalysts promoted with Ca (Gotti & Prins 1996, 1998), Pd/SiO$_2$ catalysts promoted with Na (Liotta *et al.* 1996), Pt/SiO$_2$ catalysts promoted with Ca (Watling *et al.* 1999) and Rh/SiO$_2$ catalysts with La (Borer &

Prins 1993) have shown that the noble metal and the promoter are in close contact. On the other hand, it was found that the irreversible amount of chemisorbed CO at a very high loading of promoter over Pd/SiO$_2$, Li/Pd atomic ratio equals 4, was higher than that for the base catalyst (Kazi *et al*. 1995). However, using a TEM technique, the average Pd particle size was not found to decrease upon Li doping. For this loading of promoter, it was found that the rate of methanol synthesis was lower than that for the base catalyst, which was related to physical blockage of Pd by the promoter (Kazi *et al*. 1995).

Thus, up to relatively moderate levels of Ca doping (depending on the type of materials and the method of preparation used), the observed decrease in the CO uptake is suggested to be due to the location of Ca in the neighborhood of Pd that would probably interfere with the chemisorption outcomes to some extent. With higher levels of Ca doping of Pd/SiO$_2$, the increase in the CO uptake is suggested to be due to other reasons than the enhancement of Pd dispersion, as might be expected by referring to the technique used for the preparation of promoted catalysts in this study. For high Ca loading levels, it is suggested that the exposed Pd surface is partially blocked by the promoter and/or large islands of gathered promoter species, as found in the case of Li/Pd/SiO$_2$ (Kazi *et al*. 1995) and Cu/ZnO/SiO$_2$ (Bailie *et al*. 1995), while a significant part of these species might lie on the support (Rieck & Bell 1986). Thus, the increase in the CO uptake in this case could be due to the direct interaction of the chemisorbed gas with the promoter itself, which is located on the exposed surface of Pd and/or on the support. On the other hand, using different methods of preparation of alkaline earth-promoted Pd catalysts may actually increase Pd dispersion in some cases as reflected by the increase in the chemosorption capacity of Pd and proved by means of other experimental techniques, but this issue is the focus of another study under development in our lab.

The total rates of CO hydrogenation for both the Ca/Pd/S1 and the Ca/Pd/S2 catalyst series had their maximum values at moderate levels of Ca (Table 3). For the Ca/Pd/S2 catalyst series with Ca levels of 1.0 and 2.0 wt %, the overall activities were lower than that for the base catalyst, Pd/S2. Therefore, the addition of Ca to Pd/SiO$_2$ up to a moderate level results in the increase in the overall activity of the Pd catalyst for CO hydrogenation. However, by increasing Ca content, the results suggest that part of the active surface of the catalyst was physically blocked by the promoter, resulting in the observed decrease in the overall activity for CO hydrogenation.

Because of the nature of the catalyst precursor (PdCl$_2$) and promoter precursor (CaCl$_2$) used to prepare the catalysts under investigation, it might be thought that the removal of Cl$^-$ from the catalyst surface during reaction in this work would affect the performance. Narita *et al*. (1987), in fact, have found that

treating Pd/SiO$_2$ prepared from PdCl$_2$ with H$_2$ at 177°C before reaction removes essentially all Cl$^-$ from the catalyst because Cl$^-$ is not included in the structure of SiO$_2$. Thus, treating the Pd/SiO$_2$ catalysts in this study with H$_2$ at 400°C prior to reaction would probably remove all residual Cl$^-$. This does not mean that using Pd precursor containing Cl$^-$ would not have any indirect impact on the activity of these catalysts for methanol synthesis. On the contrary, it has been shown (Deligianni *et al.* 1985, Kelly *et al.* 1986, Ali & Goodwin 1998) that catalysts prepared using PdCl$_2$ have more activity than the ones prepared using Pd(NO$_3$)$_2$. However, in this investigation, by fixing the type of catalyst and promoter (both contained Cl$^-$) and pretreating the catalysts with H$_2$ prior to reaction (at the previous mentioned specified conditions) it can be concluded that Cl$^-$ does not act as a variable between one catalyst to another, especially in terms of the performance during reaction.

The product selectivities were altered by Ca promotion as shown in Fig. 1. Maximum methanol selectivity was at the moderate loading of Ca used in this investigation, where the highest methanol selectivity was 74% at Ca/Pd atomic ratio of 0.93. Thus, Ca presence has a significant effect on the selectivity for methanol formation as found by others (Hahm & Lee 1990, Gotti & Prins 1996). However, many factors would effect the extent of this observed impact, such as the materials, methods of preparation and pretreatment used for catalyst preparation.

For both catalyst series studied in this investigation, the rate of methanol formation was enhanced for the promoted Pd catalysts having relatively low to moderate levels of Ca (Table 3). Over this range of Ca loading, the average site activity for CH$_3$OH formation (TOF$_{CH3OH}$) was enhanced significantly. This observed increase in the TOF$_{CH3OH}$ is attributed to the presence of the promoter, which is directly involved in methanol synthesis. The trend of the change of methanol rate versus promoter loading observed in this study (volcano trend) was in agreement with the one reported for the promotion of Pd for methanol synthesis over a wide range of Li loading levels up to a Li/Pd atomic ratio of 4 (Kazi *et al.* 1995). The catalysts prepared in this referenced study and this work were similar in terms of an important aspect, which is the sequence of impregnation of promoter and Pd over SiO$_2$ (impregnating of promoter over supported Pd over SiO$_2$). The impregnation of supported Pd with high levels of promoter resulted in blocking some of the active surface, which was the reason behind the observed decrease in the rate of methanol formation.

The parameters obtained in this investigation, with respect to the dependence of the rate of methanol synthesis on the partial pressures of H$_2$ and CO for Pd/S1, were $+0.57$ and $+0.34$, respectively, while for 0.7Ca/Pd/S1 were $+0.94$ and $+0.29$, respectively. The reported parameters in the literature for methanol

synthesis with respect to H$_2$ and CO were different than those found here. The orders with respect to H$_2$ and CO for methanol synthesis over Pd/SiO$_2$ were found to be equal to +2.19 and either -0.44 or -1.14, respectively, (Fajula *et al.* 1982), while another study show these values were +0.75 and +0.15, respectively, (Hicks & Bell 1985). The differences observed in the power law expressions are attributed to many factors such as the differences in the precursors and support types used, and the methods of preparation and pretreatment applied. Thus, varying any of the factors mentioned above would alter methanol synthesis. This could be the reason for the controversial behind the mechanism of methanol synthesis.

The power law expression for the rate of methanol formation, as mentioned before, varied upon Ca promotion, especially with respect to the dependence on the order of H$_2$. This could be due to the change in the strength of H$_2$ adsorption on the catalyst because of the presence of the alkaline earth. Thus, one of the impacts of alkaline earth promotion could be on the H$_2$ adsorption capability of Pd/SiO$_2$, which was reflected on the activity of Pd for CO hydrogenation. It has to be mentioned that there are many proposed mechanisms by which methanol is formed from a CO hydrogenation reaction on Pd catalysts. Kikuzone *et al.* (1981) suggested that methanol formation from the reaction of CO and H$_2$ on Pd catalysts might be due to the hydrogenation of formate ion. Improvements in the activity were noticed by the addition of promoters (such as Na$^+$), which was suggested to be due to the presence of the promoters close to Pd particles or ions (Kikuzono *et al.* 1981). Driessen *et al.* (1983) suggested that Mg and La promote methanol synthesis of Pd/SiO$_2$ catalysts by the stabilization of the Pd^0 (source of reducing species) in the neighborhood of Pd^{n+} (active centers for the formation of methanol). For Pd supported on rare earth oxides, Sudhakar & Vannice (1985) proposed that methanol is formed through formyl/formate intermediates. Vannice *et al.* (1987) found that a relationship exists between the basicity of the rare earth oxides and the TOF$_{CH3OH}$, which uphold a mechanism for the formation of methanol through formate intermediates from the reaction of CO and H$_2$ over Pd supported on rare earth oxides. Sellmer *et al.* (1997) studied the effect of promoter on methanol synthesis over Pd/SiO$_2$ by means of XPS/SIMS and identified surface formate and methoxy species in addition to CaSiO$_3$. Gotti & Prins (1998) proposed that for Pd supported on SiO$_2$ methanol is formed via the formation of formate intermediates which is enhanced by the formation of CaO-Pd active interface.

It can be seen from all that have been discussed that the enhancement in the TOF$_{CH3OH}$ due to Ca loading at low to moderate levels was combined by a decrease in CO chemisorption with is suggested to be related to the interaction

of Ca and Pd. Thus it can be suggested that the presence of Ca near the Pd particles would directly influence methanol synthesis of supported Pd on SiO_2. However, at high Ca loading levels, the disappearance of the positive impact of the promoter as reflected by the decrease in the TOF_{CH3OH} was suggested to be due to the physical blockage of part of the active surface of the catalyst by the promoter.

Imapct of Varying SiO_2 Support

The catalyst activity and selectivity toward CO hydrogenation in this investigation was found to be altered by the type of the support used. The studies done by Kikuzono *et al.* (1981), Ryndin *et al.* (1981), Fajula *et al.* (1982), Deligianni *et al.* (1985), cavalcanti et al. (1992) and Ali & Goodwin (1998) have found similar effect. The results reported by Fajula *et al.* (1982) show that the type of SiO_2 support used to prepare Pd catalysts had significantly altered the activity and the selectivity toward CO hydrogenation. The findings of Deligianni *et al.* (1985) also supports this point, where the rate of methanol formation was changed by altering the type of SiO_2 support (Pd catalysts prepared using SiO_2 type Davison grade 59 had more activity for methanol formation than when using SiO_2 type Davison grade 57).

Many investigators found the acidity of the support alters the activity of Pd for CO hydrogenation (Kikuzono *et al.* 1981, Ryndin *et al.* 1981, Fajula *et al.* 1982, Cavalcanti *et al.* 1992, Ali & Goodwin 1998). Dimethyl ether (DME) is known to be produced from methanol on acidic sites of supports such as Al_2O_3 and $SiO_2-Al_2O_3$ (Rynding et al. 1981, Ali & Goodwin 1998). However, due to the lack of acidic sites of sufficient strength in the supports used in this work (SiO_2), DME was not produced.

Although a study of Pd supported on different SiO_2 supports showed that there is no relationship between CO hydrogenation activity of Pd/SiO_2 catalysts and the metal ion impurities existing in the supports (Kelly *et al.* 1986), it is known that certain metals such as the ones of group IA and IIA have promoting effect on Pd for CO hydrogenation, particularly for methanol synthesis (Kikuzono *et al.* 1981, Driessen *et al.* 1983, Deligianni *et al.* 1985, Kelly *et al.* 1986, Hahm & Lee 1990, Kazi *et al.* 1995, Gotti & Prins 1998). Many of these metallic atoms are typically present as impurities in support materials, as is the case here (Table 1). As metioned in the result section, SiO_2 type Davisil grade 644 had higher levels of Na, Mg and Ca impurities than SiO_2 type Davisil grade 634.

It appears that due to the transfer of these impurities from the support to the metal surface during catalyst preparation and reaction (Gotti & Prins 1998), the

presence of these impurities with their tabulated levels would affect to different degrees the activity of Pd catalysts for CO hydrogenation. Due to the differences in the levels of impurities in the supports used (SiO$_2$ grade 634 and 644), the overall rate of CO hydrogenation (Table 3) for the Pd/S2 base catalyst was slightly higher than that for the other base catalyst (Pd/S1), while the average site activity for the formation of methanol (TOF$_{CH3OH}$) was significantly higher for the Pd/S2 base catalyst than for the other base catalyst. However, no conclusion can be stated about the possible effect of the difference in the surface area between these two supports (SiO$_2$ type Davisil grade 634 have higher surface area than SiO$_2$ type Davisil grade 644, 480 m^2/g versus 300m^2/g, respectively) on the performance of the catalysts during CO hydrogenation reaction. This is because the level of impurities in both supports were also different.

CONCLUSIONS

Ca had a significant promoting effect on Pd/SiO$_2$ for CO hydrogenation to methanol. The increase in the rate of methanol formation upon Ca addition over Pd/SiO$_2$ was not combined with a similar effect on the production rate of hydrocarbons (methane and ethane). The highest values of the average site activity for methanol formation (TOF$_{CH3OH}$) were at low to moderate levels of Ca loading. The TOF$_{CH3OH}$ for the Ca/Pd/S1 catalyst series increased from 1.8 (for the Pd/S1 base catalyst) to 4.1 (for the 0.7Ca/Pd/S1 catalyst), while for the other catalyst series it increased from 3.1 (for the Pd/S2 base catalyst) to 5.8 (for the 0.4Ca/Pd/S2 catalyst). This enhancement in the TOF$_{CH3OH}$ due to Ca doping suggested that it was related to the direct involvement of the promoter in methanol synthesis. On the other hand, the addition of high levels of Ca over Pd/SiO$_2$ (equal 1.0 wt % or higher) was found to have a negative impact on the activity of the catalyst. This decrease in the rate of CO hydrogenation and especially the methanol formation rate suggested a relationship to the partial blockage of the active sites by the promoter. The differences in the levels of metallic impurities having potential promoting effect in the SiO$_2$ supports used (higher concentrations of Na, Mg and Ca impurities were present in SiO$_2$ type Davisil grade 644 than SiO$_2$ type Davisil grade 634) was suggested to account for some of the variations of the catalytic behavior of the catalysts considered. The TOF$_{CH3OH}$ for the base catalyst prepared using SiO$_2$ grade 644 (Pd/S2) was higher than that for the other base catalyst using SiO$_2$ grade 634(Pd/S1), 3.1 versus 1.8, respectively.

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تأثير كمية الكالسيوم ونوعية السيليكا على فاعلية البلاديوم لهدرجة أول أكسيد الكربون لانتاج الميثانول

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خلاصة

إن تأثير التعزيز بالكالسيوم للبلاديوم (النسبة الوزنية تساوي 2 في المائة) المحمل على السيليكا على هدرجة أول أكسيد الكربون لانتاج الميثانول قد بحث باستخدام مستويات مختلفة من الكالسيوم (حتى نسبة وزنية تساوي 2 في المائة) ونوعين من قواعد السيليكا (دافيسيل درجة 634 ودرجة 644). لقد وجد أن الكالسيوم له تأثير تعزيزي انتقائي على البلاديوم لهدرجة أول أكسيد الكربون لتكوين الميثانول. إن أعلى زيادة لمتوسط كفاءة موقع تكوين الميثانول قد وجد عند التحميل بنسب منخفضة إلى متوسطة من الكالسيوم (نسب وزنية تساوي 0.4 إلى 0.7 في المائة)، وعز ذلك إلى التضمن المباشر للمادة المعززة في عملية تكوين الميثانول. ولكن، التحميل بأكثر من نسبة وزنية تساوي 0.7 في المائة من الكالسيوم نتج عنه نقص فعالية البلاديوم كمادة حفازة وذلك باحتمال سد الكالسيوم الجزئي للسطح الفعال للمادة الحفازة. إن نوعية السيليكا كقاعدة، من جهة أخرى، قد وجد لها بعض التأثير على فعالية البلاديوم لهدرجة أول أكسيد الكربون. وعز ذلك للفروقات بمستويات الشوائب المعدنية الموجودة (الصوديوم، المغنيسيوم والكالسيوم) والتي من الممكن أن يكون لها تأثير تعزيزي (سيليكا درجة 644 تحوي تركيز أكبر من هذه الشوائب مقارنة مع سيليكا درجة 634).