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RESEARCH NOTE

Alloy Formation in Li-Promoted Pd/SiO_2 Catalysts for the Synthesis of Methanol

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Li-promoted Pd catalysts are active for the synthesis of methanol from synthesis gas and exhibit properties that can be explained by alloy formation. The relative partial Gibbs energy of Li in a solid solution of Li and Pd is very exergonic at a low molar fraction of Li, but much less exergonic at higher concentrations. Therefore, when Li-promoted Pd/SiO_2 catalysts are reduced in hydrogen, a reduction of Li^+ to Li^0 to yield a Li–Pd alloy only proceeds to a low degree, dependent on the temperature and the purity of the hydrogen. This explains a constant hydrogen chemisorption capacity of Li/Pd/SiO_2 catalysts at a high Li loading. The properties of Ca-promoted Pd catalysts can be explained by alloy formation as well.

Key Words: **palladium; lithium; calcium; promoter; chemisorption; FTIR; strong metal-support interaction.**

INTRODUCTION

Palladium on a silica support is a very active and selective catalyst for the synthesis of methanol from carbon monoxide and hydrogen, if a suitable promoter is added. A former investigation in our laboratory showed that Li was the most effective promoter among the alkali metals (1). Ca-promoted Pd catalysts showed the highest activity and selectivity of all catalysts prepared from alkali and alkaline earth promoters.

To find out more about the interaction of Ca and Pd, the Ca-promoted Pd catalysts were investigated by a variety of techniques (2), including catalytic activity measurements, selective chemisorption of H_2 and CO, temperature-programmed reduction (TPR), and IR spectroscopy of CO adsorbed on the reduced catalysts. From TPR results we concluded that the Ca promoter migrated toward the PdO particles during the preparation of the catalysts and formed a shell of the mixed oxide $CaPd_3O_4$ (bronze) around these particles. The selective chemisorption of H_2 and CO showed that the presence of Ca on the reduced catalysts lowered the number of adsorption sites by about one third compared to the unpromoted sample at a very low Ca loading and remained constant at a higher Ca loading. We explained the constant chemisorption capacities by a limited amount of Ca on the reduced Pd particles. We could not explain, however, why one Ca atom was able to block approximately 25 adsorption sites on the catalyst with the lowest Ca loading (Ca : Pd ratio = 0.004). We speculated that the reason might be a change in the electronic properties of the Pd, but at that time we excluded the formation of an alloy, since thermodynamic calculations showed that less than one Ca atom in a mole would be reduced from Ca^{2+} to Ca^0. Also the IR spectra of adsorbed CO on the reduced catalysts changed after addition of the Ca promoter. The bands due to linearly and bridge-bonded CO were shifted to lower wave numbers and a new band at 1600–1900 cm^{-1} appeared, which had previously been assigned to CO molecules bonded to Pd with the C atom and to a promoter cation with the O atom (3–5). Since we excluded alloy formation, we speculated that this band at 1600–1900 cm^{-1} was an artefact. Activity data for the hydrogenation of CO showed that the production of methane was suppressed at a low Ca loading. We explained this by Ca species that block the sites, which are necessary for the dissociation of CO to yield methane.

Recently we came across thermodynamic data for the formation of an alloy from Li and Pd at a low concentration of Li at 750 K (6), which is close to the reduction temperature in our experiments (723 K). We will use these data to show that alloy formation may occur during reduction of Li-promoted Pd catalysts. A search for other Pd-promoter systems, which form alloys was unsuccessful. The reason may be that the thermodynamics of alloy formation from Pd and other promoters have only been determined at high temperatures or relatively high molar fractions of the promoters (7–14), where alloy formation is less exergonic. Only the heats of the formation of alloys at typical reduction temperatures and very low molar fractions could confirm alloy formation of Pd and promoters other than Li.

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We will report the selective chemisorption of hydrogen and the catalytic activity in the hydrogenation of CO for a series of Li-promoted Pd catalysts and compare the results with those obtained formerly for a series of Ca-promoted Pd catalysts (2). In addition, we will discuss the results for the Ca–Pd system with respect to possible alloy formation.

EXPERIMENTAL

$Li/Pd/SiO_2$ samples were prepared by a two-step pore volume impregnation of a silica support. To avoid the presence of impurities as on commercial supports, we prepared our own silica (~900 $m^2\ g^{-1}$) by hydrolysis of tetraethoxysilane (Fluka, puriss. >99%) (15). The silica was first impregnated with an aqueous solution of $[Pd(NH_3)_4](NO_3)_2$ (Johnson Matthey), dried at 393 K for 16 h (1 K min^{-1}), and calcined in air at 723 K (10 K min^{-1}) for 2 h to give a PdO/SiO_2 sample with a loading of 4.5 wt% Pd. A subsequent impregnation with an aqueous solution of $LiNO_3$ (Fluka, MicroSelect >99%), followed by the same drying and calcination procedure, gave $Li/PdO/SiO_2$ samples with molar Li : Pd ratios from 0.005 to 0.5.

The catalysts were tested for the hydrogenation of CO at 553 K and 2.5 MPa in a microflow reactor. The samples (340 mg) were reduced in a flow of H_2 (30 ml min^{-1}) at atmospheric pressure and 723 K (5 K min^{-1}) for 1 h. After the samples were cooled to reaction temperature (553 K), the pressure was increased to working pressure (2.5 MPa) before the CO was added. The total flow of the reactants was 0.11 mol h^{-1} at a $H_2 : CO$ ratio of 2. Experiments were performed for 24 h and products were analysed every hour using two online gas chromatographs.

The amount of irreversibly adsorbed hydrogen was determined by the static volumetric chemisorption method. The catalysts (2 mg) were reduced in a flow of H_2 (30 ml min^{-1}) at 723 K (5 K min^{-1}) for 1 h and then evacuated at 10^{-4} Pa for 1 h at the same temperature to remove any H_2. The isotherms were measured at 293 K and below 1.2 k Pa to avoid the formation of β-palladium hydride (16). To distinguish between the amount of irreversibly and reversibly adsorbed H_2, the sample was outgassed at 10^{-4} Pa and 293 K for 35 min before a second isotherm was measured (17, 18).

The catalysts were prepared and characterised under identical conditions as in our previous investigations (1, 2).

RESULTS

Catalytic Activity

The catalytic activity of a series of Li-promoted Pd catalysts was measured for the hydrogenation of CO at 553 K and 2.5 MPa. The catalytic data of the Pd catalysts, containing various amounts of Li, are presented in Fig. 1 and Table 1. While pure Pd on SiO_2 showed only a modest activity for methanol, the addition of Li resulted in a strong increase in the methanol activity, which levels off at a higher Li : Pd ratio.

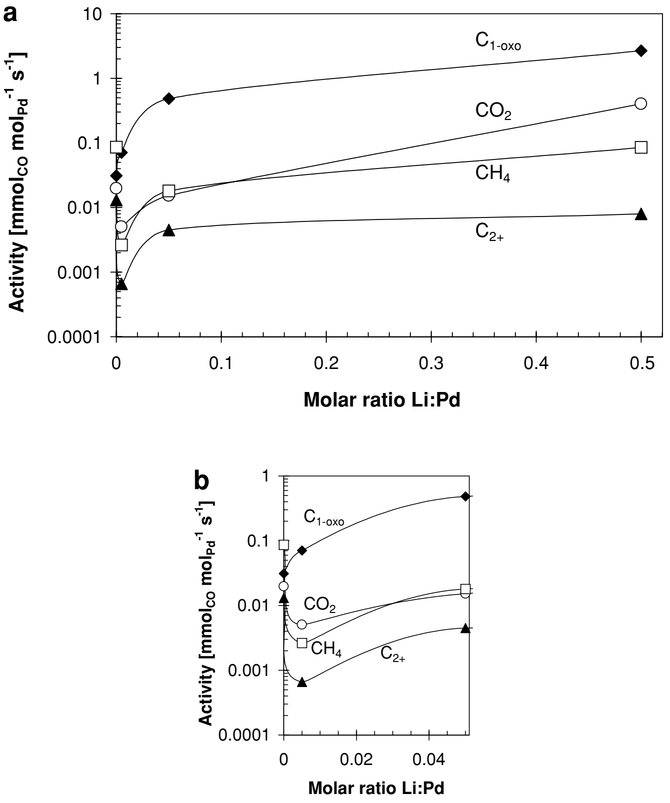

FIG. 1. (a) Product yields of $C_{1\text{-oxo}}$ (methanol and dimethyl ether), CO_2, CH_4, and C_{2+} (alkanes and alkenes with two or more carbon atoms) over Pd catalysts containing different amounts of Li. Figure 1b displays the yields at low Li : Pd ratios.

The methane activity decreased upon addition of Li, passed through a minimum at a Li : Pd ratio of 0.005, and increased at a higher Li loading, following the trend of the methanol activity (Fig. 1). Apparently Li modifies the Pd in such a way that breaking the C–O bond in carbon

TABLE 1

Catalytic Activities and Selectivities of Li-Promoted Pd/SiO_2 Catalysts

Li : Pd (molar)	Total activity[a]	Selectivity (%)[b] $C_{1\text{-oxo}}$	CH_4	C_{2+}	CO_2	MeOH : DME[c]
0	0.15	20.7	57.3	8.7	13.2	1.5
0.005	0.08	88.5	3.4	1.0	6.5	6
0.05	0.52	92.8	3.5	0.9	3.0	15
0.5	3.18	84.4	2.7	0.3	12.6	60

[a] Activity in $mmol_{CO}\ mol_{Pd}^{-1}\ s^{-1}$.

[b] Selectivity for $C_{1\text{-oxo}}$ (methanol and dimethyl ether), CH_4, C_{2+} (alkanes and alkenes with 2 or more carbon atoms), and CO_2.

[c] Methanol to dimethyl ether ratio.

monoxide becomes more difficult and less methane is produced. The increase in methane activity at a higher Li loading might be explained by a secondary reaction of methanol to methane. Kester *et al.* (19) reported a higher methane activity over Pd/La_2O_3 catalysts than over Pd/SiO_2. They concluded from temperature-programmed reaction experiments that methoxy species, which were adsorbed on the La_2O_3 support, became easily hydrogenated by hydrogen atoms that were spilled over from the Pd.

The C_{2+} activity followed the same trend as the methane activity, albeit one order of a magnitude lower. Mainly ethane was produced, and the higher alkanes showed a Schultz–Flory distribution. Also the activity for ethane was initially suppressed by addition of Li, but increased at a higher Li loading. This increase might as well be explained by a secondary reaction of methanol to higher alkanes. The curve displaying the activity for CO_2 looks similar to that for the methanol activity.

Hydrogen Chemisorption Capacity

The chemisorption capacities for catalysts of various Li loadings are presented in Fig. 2. The pure Pd/SiO_2 catalyst had a dispersion of 24% and addition of a very small amount of Li resulted in a reduction in the fraction of exposed Pd atoms to 21% for the 0.005 Li–Pd sample and remained constant at 19% at a higher Li loading.

The Pd particle size distribution will not change upon impregnation of PdO/SiO_2 with an aqueous solution of $LiNO_3$ and subsequent drying and calcination, since PdO is insoluble in water. For Ca-promoted Pd catalysts, we demonstrated by electron microscopy that the Pd particle size distribution was not influenced by the presence of the promoter (2). Therefore, the reduced hydrogen chemisorption capacities of the Li-promoted Pd catalysts cannot be due to a lower Pd dispersion and must be due to the presence of the Li promoter. This means that one Li atom blocks approximately six Pd atoms for the chemisorption of H_2 in the 0.005 Li–Pd sample (0.005 Li block 0.03 Pd), if we assume that all Li is present on the Pd particles after reduction.

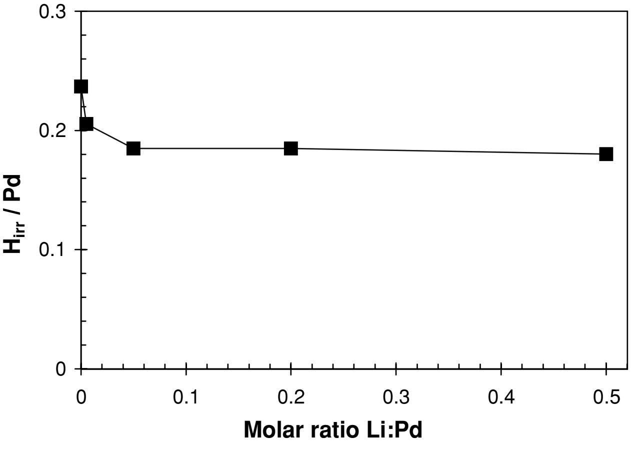

FIG. 2. Amount of irreversibly chemisorbed H atoms per total number of Pd atoms.

DISCUSSION

Li and Li compounds have properties different from their homologues in group 1 of the periodic table and rather behave like the compounds of the group 2 element Mg. Thus it is not surprising that Li- and Ca-promoted Pd catalysts show very similar product distributions and activities for the hydrogenation of CO as well as a similar trend for the chemisorption capacity of H_2.

Both promoters, Li and Ca, have a strong promoting effect at a low loading, which levels off at a promoter : Pd ratio greater than 0.05 to 0.1, respectively. The activity for methane and for higher alkanes goes through a minimum at a promoter : Pd ratio of about 0.005 and increases again at a higher loading, following the trend of the methanol activity. Also the activity for CO_2 is very similar for both catalyst series and increases with the promoter loading, though it passes through a minimum in the Li-promoted series, albeit at a very low activity.

The curves describing the chemisorption results of the Ca-promoted Pd series have a pronounced L-shape. The H_2 and CO chemisorption capacities of pure Pd on silica (33%) decrease to 22 and 20%, respectively, at a Ca : Pd ratio of 0.004 and remain at 20% at a higher Ca loading. A very similar L-shaped curve is found for the hydrogen chemisorption of the Li-promoted Pd catalysts. The initial dispersion of 24% decreases to 21% for 0.005 Li–Pd and remains constant at 19% at a higher Li loading.

The H_2 chemisorption results indicate that one Li atom blocks six chemisorption sites on Pd for the sample with the lowest Li content (0.005 Li–Pd), while on a 0.004 Ca–Pd catalyst sample one Ca blocked approximately 25 sites (2). From a geometric point of view one Ca species, e.g., CaO, cannot block 25 adsorption sites. It was proposed that Ca species are adsorbed on kink and corner sites of the Pd particles. Since these sites are necessary for the dissociation of H_2, no H_2 will be chemisorbed on Pd particles where the promoter blocks all these sites. This model cannot explain, however, why the hydrogen chemisorption is suppressed to a limited extent only, even at higher Ca : Pd ratios. Furthermore, since the results of the selective chemisorption of CO were almost identical to the results of the H_2 chemisorption, this model can be ruled out, because CO adsorbs associatively and does not need kink and corner sites. It was therefore speculated that Ca might induce changes in the electronic properties of the Pd particles, which would explain the reduced chemisorption capacities for H_2 and CO.

Results from surface science might explain the decrease in chemisorption capacity. Blocking of adsorption sites for CO and H_2 has been reported when atoms of the group 1 element K were deposited on Pd single crystal surfaces. Solymosi and Kovacs calculated that each K atom is capable of blocking four to five adsorption sites for H atoms on a Pd(100) surface (20). Also the chemisorption of CO was shown to decrease continuously with increasing amounts of K adatoms on Pd(100) (21). The major difference between their model system and our supported catalysts is that metallic K was deposited onto the Pd(100) surfaces, while our PdO/SiO_2 samples were impregnated with the corresponding precursor salts, and Li or Ca were initially present as Li^+ or Ca^{2+} after catalyst preparation.

Since also the work function of Pd(100) decreases with increasing K coverage (22), it is evident that the electronic properties of the surface play an important role in the adsorption and desorption behaviour of H_2 and CO. After a thermal desorption experiment up to 1100 K, not all potassium had been desorbed, but an amount corresponding to 5% of a monolayer was still detected by Auger electron spectroscopy (22). An explanation of these results might be alloy formation in the surface region of the Pd.

Binary alloys of group 10 metals (Ni, Pd, Pt) and electropositive metals, such as the alkali metals, the alkaline earth metals, Al, Zr, the lanthanides, and the actinides, are known and their formation from the elements is very exergonic (6–8, 10, 11, 13, 14). The thermodynamics of these alloys depend strongly on the composition. The relative partial Gibbs energy of the electropositive metal i (ΔG_i) becomes more negative with decreasing concentration. Relative partial excess Gibbs energies of Al, Y, Ce, Nd, Gd, and Th at infinite dilution of these elements in Pd range from -260 to -405 kJ mol^{-1} (10). Also the temperature dependence of ΔG_i in this type of binary alloy can be considerable, especially at a low concentration of the electropostive metal i. The lower the temperature, the more exergonic ΔG_i is (8, 10, 12, 14). Hitherto the thermodynamics of a solid solution of Ca in Pd at a low molar fraction of Ca have only been determined at 1073 K (9), while ΔG_{Li} for the Li–Pd system is known at 750 K (6).

The equilibrium constant for the reduction of Li_2O by H_2 in the presence of Pd to give water and a solid solution of Li in Pd (Eq. [1]) at 723 K was calculated according to Eqs. [2] and [3], where ΔG_r^{723} is the free Gibbs energy of reaction (1), $\Delta G_{f,\mathrm{H_2O}}^{723}$ the free Gibbs energy of the formation of H_2O, $\Delta G_{f,\mathrm{Li_2O}}^{723}$ the free Gibbs energy of the formation of Li_2O, and $\Delta G_{\mathrm{Li}}^{723}$ the relative partial Gibbs energy of Li at infinite dilution in Pd.

$$\frac{1}{2}\mathrm{Li_2O} + \frac{1}{2}\mathrm{H_2} + x\mathrm{Pd} \rightarrow \mathrm{LiPd}_x + \frac{1}{2}\mathrm{H_2O}\ (x \rightarrow \infty) \quad [1]$$

$$\Delta G_r^{723} = \frac{1}{2}\left(\Delta G_{f,\mathrm{H_2O}}^{723} - \Delta G_{f,\mathrm{Li_2O}}^{723}\right) + \Delta G_{\mathrm{Li}}^{723} \quad [2]$$

$$K = \frac{[\mathrm{LiPd}_x] \times [\mathrm{H_2O}]^{\frac{1}{2}}}{[\mathrm{Li^+}] \times [\mathrm{H_2}]^{\frac{1}{2}}} = \exp\left(\frac{-\Delta G_r^T}{\mathrm{RT}}\right). \quad [3]$$

The Gibbs energies of formation of Li_2O and H_2O at 723 K were calculated using tabulated values (23). $\Delta G_{\mathrm{Li}}^{723}$ was taken to be -120 kJ mol^{-1}, the value determined by Widulle at 750 K (6). If the amount of water and the equivalent of oxygen in high purity H_2 (99.9990%) is assumed to be 5 ppm, then the $\mathrm{LiPd_x/Li^+}$ ratio is calculated to be about 5, which means that alloy formation is possible at a low concentration of Li in Pd. Since $\Delta G_{\mathrm{Li}}^{723}$ becomes less exergonic with increasing molar fraction of Li in Pd, alloy formation only proceeds to a certain Li : Pd ratio at a given temperature. As a consequence, the Li : Pd ratio in the alloy is independent of the overall Li loading of the catalyst and so is the chemisorption capacity of H_2, which depends on the Li content in the alloy. The degree of alloy formation depends on the purity of H_2 and the reduction temperature, according to Eq. [3]. The temperature dependence of ΔG_r^T needs to be considered as well, since ΔG_{Li} becomes less exergonic at higher temperature.

The extraordinary stability of binary alloys of a very electropositive metal and Pd, along with the strong deviation of thermodynamics from ideal at low concentration, was ascribed to a charge transfer of the valence electrons of the electropositive component to the electron gas of the alloy (10, 12). This charge transfer might be stronger for the group 2 element Ca than for the group 1 element Li and explain why Ca blocks more adsorption sites than Li.

In an earlier investigation of Pd/SiO_2 catalysts with identical amounts of various promoters, we found that the stronger the suppression of the hydrogen chemisorption capacity, the higher was the methanol activity (2). These results indicate that alloy formation, accompanied by a change in the electronic properties of the noble metal and a suppression of the chemisorption, might be essential for the promotion to occur. A stronger back donation to the $2\pi^*$ orbital of CO might increase the hydrogenation rate to methanol by facilitating the insertion of CO molecules into O–H bonds on the promoter to give formate species, which are believed to be intermediates in the synthesis of methanol over Pd (1). In addition, we propose that alloy formation in our Li- and Ca-promoted Pd/SiO_2 catalysts caused the suppression of the methane activity at a low promoter loading. The influence of the work function of noble metals on their catalytic performance is known. Tracey *et al.* (24) showed a pronounced change in activity and selectivity for the hydrogenation of acetylene over a Pt catalyst by the non-Faradaic electrochemical modification of catalytic activity. The kinetics of hydrogenation reactions over promoted Pt group metals will not only depend on the temperature due to the temperature dependence in the Arrhenius equation, but also depend on the temperature dependence of the equilibrium of alloy formation, since the activation energy will change with the work function.

A further indication for alloy formation in Ca-promoted Pd catalysts comes from FTIR-spectra of adsorbed CO on these samples (2). The IR bands due to linear and bridge-bonded CO were shifted to lower wave numbers on Ca-promoted Pd catalysts compared to pure Pd on SiO$_2$. In addition, bands in the region from 1600 to 1900 cm^{-1} appeared in the spectra of the Ca-promoted samples. These bands were formerly ascribed to CO molecules, which are bonded with the C atom to a Pd atom, while the O atom is bonded to a promoter metal cation (3–5). An alternative explanation would be that these bands arise from a charge transfer from the Ca atoms to the $2\pi^*$ orbitals of the CO molecules adsorbed on Pd atoms next to Ca atoms. Bands of adsorbed CO at wave numbers from 1500 to 1900 cm^{-1} have been observed on single crystals when CO and K were coadsorbed on Pt(111) (25, 26).

Alloy formation might also explain some of the features associated with the strong metal-support interaction (SMSI) behaviour, such as the suppression of the chemisorption (5, 27, 28), changes in the IR spectra (3–5), and changes in the binding energy of XPS spectra (27, 28). Already Tauster *et al.* speculated that alloy formation might be an explanation for these phenomena (29, 30), although for metals supported on TiO$_2$, the most prominent example of the SMSI behaviour, it was unambiguously demonstrated that the metal particles become encapsulated by the support (31, 32).

There is no need for the formation of intermetallic compounds of defined stoichiometry, since the formation of solid solutions containing a very low amount of an electropositive element seems to be sufficient to alter the electronic properties of the surface of a platinum-group metal and therefore its catalytic properties. We believe that alloy formation occurs more frequently in metallic catalysts under reductive conditions than is generally assumed. The heats of formation of alloys at typical reaction temperatures and very low molar fractions of the electropositive metal may provide an answer.

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