

POSSIBLE RELATIONSHIPS OF SITES FOR CO ADSORPTION WITH METHANOL
SYNTHESIS ACTIVITY OF SUPPORTED Pd CATALYSTS

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Pd/SiO₂ catalysts with and without promoters for methanol synthesis have been previously studied (1-6), with partially contradictory conclusions. Lunsford, et al. (3), concluded that Pd structural effects play an important role in the activity of the catalyst, since catalysts with small Pd crystallites produce methanol while larger crystallites produce methane. Such structural effects can be induced by different grades of silica support. On the other hand, Ponec, et al. (1,6) believe that electronic factors are more important and Pd II "ions" are the centers for CO activation. The number of such sites is presumably increased by the presence of alkali metals. The effect of alkali metals such as Li appears to be more complex (1,5). Whatever the nature of the active centers, the addition of basic metals as well as the use of basic supports (4) promotes reactivity.

EXPERIMENTAL

The reactor used in testing the methanol synthesis catalyst was a vertical 1/2" stainless steel tube enclosed in a hinged furnace. Cylinder CO and H₂ were fed into the system via pressure regulators and Brook's mass flow controllers. The desired pressure was maintained at the reactor outlet by a pneumatically operated research control valve. Outlet flows were measured by a wet test meter.

Four grams of vacuum-dried catalyst (14-20 mesh) were diluted (if necessary) to a 10 cc volume with α -alumina particles and placed centrally in the reactor. The catalyst was pretreated in situ by passing N₂ at 150°C for 30 minutes, and then passing H₂ at 340°C for 1 hour. Activities were measured after two hours running in a H₂/CO feed of mole ratio 2/1.

Infrared analysis were performed on a computerized IR Beckman 4260 as previously described (7). Corrections were applied for changes in background bands (arising from the support) caused by cooling of the sample when CO was admitted to the cell. Some spectra were recorded with a Perkin-Elmer 1550 FTIR spectrometer.

The catalysts were prepared using two different batches of Davison silica gel, 57 and 59.

Impregnated catalysts were prepared by the incipient wetness technique. Pd ion exchanged catalysts were prepared by the following procedure: The required amount of Pd (NH₃)₄(NO₃)₂ solution was added to a slurry of the mixture gel and water. The water was alkalinized by adding a few drops of NH₄OH to make the pH ~9.5. After mixing for 1 hour, the silica was washed and filtered and, finally, calcined at 300°C for 2 hours. For the Li doped samples, Li was added as the hydroxide prior to the Pd impregnations.

RESULTS AND DISCUSSION

Activity Measurements

The reproducibility of activity measurements by the reactor was tested and found to be about $\pm 20\%$ of the absolute value in terms of CO converted.

Some preliminary results on pretreatment variations indicated that the initial activity of the unreduced Pd catalysts was half that of the fully reduced catalyst, but that on increasing time on stream, the activity approached that of the fully pretreated catalyst.

Two different batches of Davison silica, #57 and #59, were used in preparing the catalysts. Although specifications for the two were the same, there were some differences in the results observed, as shown in Table I.

Table I. Variation in Silica Support
 Conditions: 500 psig, SV = 900 hr⁻¹, 275°C
 and H₂:CO = 68.2:31.8

<u>Catalyst</u>	<u>Method of Pd Addition</u>	<u>% CO Converted to MeOH</u>
5% Pd/SiO ₂ 57	Impregnated	0.8
5% Pd/SiO ₂ 59	with PdCl ₂ solution	2.5
5% Pd/SiO ₂ 57	Ion exchanged with	1.2
5% Pd/SiO ₂ 59	Pd(NH ₃) ₄ (NO ₃) ₂	3.0
5% Pd/1.6% Li/SiO ₂ 57	Impregnated with	4.6
5% Pd/1.6% Li/SiO ₂ 59	PdCl ₂ solution	6.0

In all cases, Davison 59 showed an increase in activity over Davison 57. However, the increase was smallest with the Li promoted catalyst, suggesting the differences in activity may arise out of differences in the amount of residual alkali metal contaminant.

Differences in the mode of adding Pd to the support evidently made little difference in the activity of the catalyst as shown by the data of Table II.

Table II. Variation in Pd Addition
 Conditions: As in Table I

<u>Catalyst</u>	<u>Method of Pd Addition</u>	<u>% CO Converted to MeOH</u>
5% Pd/SiO ₂ 59	Impregnated with PdCl ₂	2.5
5% Pd/SiO ₂ 59	Impregnated with Pd(NO ₃) ₂	2.0
5% Pd/SiO ₂ 59	Ion Exchanged with Pd(NH ₃) ₄ (NO ₃) ₂	2.0
1.5% Pd/SiO ₂ 57	Impregnated with PdCl ₂	0.9
1.5% Pd/SiO ₂ 57	Impregnated with Pd(NO ₃) ₂	0.8

These data were obtained on catalysts ion-exchanged with amino nitrate complex or impregnated with either the nitrate or chloride salt.

Significant differences were observed when Li was added as a promoter.

Table III. Effect of Lithium Promotion
 Conditions: As in Table I

<u>Catalyst</u>	<u>Method of Pd Addition</u>	<u>% CO Converted to MeOH</u>
5% Pd/SiO ₂ 57	Impregnated with	0.8
5% Pd/SiO ₂ 57 + 1.6% Li	PdCl ₂	4.6
5% Pd/SiO ₂ 59	Impregnated with	2.5
5% Pd/SiO ₂ 59 + 1.6% Li	PdCl ₂	6.0
5% Pd/SiO ₂ 59	Impregnated with	2.0
5% Pd/SiO ₂ 59 + 1.6% Li	Pd(NO ₃) ₂	5.0
1.5% Pd/SiO ₂ 59	Ion exchanged with	3.0
1.5% Pd/SiO ₂ 59 + 1.6% Li	Pd(NH ₃) ₄ (NO ₃) ₂	4.3

Table III shows that Li always increased the activity for every catalyst type used. The increase, however, was smallest for the Pd ion exchanged on silica 59 possibly since without Li this catalyst had a higher activity, but, also, this smaller increase could be a result of the absence of residual alkali in the support.

Infrared Spectra

Figures 1 to 5 represent IR spectra of CO adsorbed on some of the catalyst samples whose activities were measured in attempting to relate catalyst performance to catalyst surface properties. Each spectrum is characterized by bands near 2075 and 1975 cm^{-1} corresponding to weakly-held CO previously assigned to linear and bridged bonding of CO on Pd, respectively (8). The spectra after evacuation and therefore representing strongly held CO, typically show less intense bands near 2060 and 1900 cm^{-1} , again reflecting linear and bridged CO. Additional bands can also be seen. These probably reflect various bridged CO species held on different crystal faces (8).

Figures 1 and 2 show spectra of CO on 5% Pd/SiO₂ made by impregnation of the chloride and nitrate salt respectively. Although the general features are similar, some differences are observed in relative intensities of the bands near 2075 and 1975 cm^{-1} corresponding to a weakly-held linear and bridge bonded CO. Differences can also be seen in the frequencies of bands caused by strongly-held CO remaining after evacuation. No difference was observed in the relative activities of the two catalysts, however.

Figure 3 shows spectra of CO on 1.5% Pd/SiO₂ (ex. PdCl₂) which was run on the FTIR. This was the only case where a band at 2165 cm^{-1} was detected.

Figure 4 shows the effect of Li on the CO/Pd spectra obtained for 1.5% Pd ion-exchanged on Davison 59 silica. (Note change in absorbance scale.) The spectrum of CO on the catalyst shows significant differences from those on the impregnated catalysts. A much more intense linear CO band is observed and a relatively weaker bridge-bonded CO band. No difference is seen in the linear CO bands (2060 and 2090 cm^{-1}) when Li is present. Only a slight difference exists between the bridged CO bands, yet a small increase in activity was noted. The strongly-held bridged CO bands in the 1850-1950 cm^{-1} appear to be progressively decreased in intensity and shifted to lower frequencies as Li content increases.

Figure 5 shows spectra of CO on the catalysts of Figures 1 and 2, respectively, after the addition of Li. Comparison with Figures 1 and 2 shows very little effect of Li on the CO spectra in the region above 1950 cm^{-1} . In the region below 1950 cm^{-1} , however, there was a significant increase in both weakly and strongly held bridged CO. There was a large corresponding increase in activity, by factors of 6 and 3, respectively, when Li was present.

DISCUSSION

Spectra of CO on Pd have been thoroughly discussed elsewhere (9). It was initially hoped, and expected, that among the variety of different types of bands observed for CO adsorbed on silica-supported Pd some correlation would be found with methanol synthesis activity. No obvious correlation was, in fact, apparent. Some previous speculation appears to have been excluded by the evidence, however, and possible explanations for Li promotion can be offered.

Careful attention was paid to possible adsorption of CO on Pd²⁺ ions, which would have been expected to give bands above 2100 cm^{-1} , and even, by analogy with Ni²⁺, as high as 2195 cm^{-1} (9). A band suggestive of Pd²⁺ adsorption sites was seen in only one instance. This was observed with the 1.5% Pd/SiO₂ (ex. PdCl₂) sample (Figure 3). After prereduction at 300°C and addition of CO, this catalyst showed a

very weak band at 2165 cm^{-1} which probably reflects CO held on Pd^{2+} ions. This catalyst was, however, one of the least active (see Table II). Unreduced Pd would not be expected under reaction conditions in any case, but the fact that activity was found to increase with increasing prereduction of the catalysts and, initially, with increasing time on stream strongly argues that Pd^{2+} sites are not, as postulated by Ponec, et al. (2,6), the active sites.

The infrared spectra show that Li addition has a small but definite effect on the bridged bonding of CO to Pd. Such bonding presumably occurs mainly on exposed faces of Pd crystallites. The effect could be either electronic or structural in nature. The Li, in a partial overlayer on a Pd surface, could affect the electronic properties of adjacent Pd atoms, changing their subsequent adsorption of CO. Alternatively, Li might promote exposure of crystal faces different from those normally present. The existence of an effect of Li on bridge bonding of CO does not, of course, mean that this is the factor responsible for activity promotion by Li. The data generally show no obvious correlation of activity with any particular type of CO bonding as revealed by the frequency and intensity of infrared bands arising from adsorbed CO.

The fact that wide differences in the types of CO adsorption on reduced Pd made so little difference in catalyst activity while marked differences in activity were observed on catalysts with generally similar CO adsorption sites suggests that some factor other than CO binding could well be of major importance. This could be the ability of the support to heterolytically dissociate hydrogen to form hydroxyl and hydride species on the surface. Zinc oxide is well-known for its ability to do this and evidence has also been presented that MgO and La_2O_3 can similarly dissociate hydrogen. Work in this laboratory has shown that alumina possesses a few sites which exhibit this behavior. The ability to form surface hydride may be the essential feature needed for methanol synthesis in addition to the non-dissociative adsorption of CO. The effect of Li may be to provide surface sites on silica on which such dissociation can occur more readily. Further work is planned to investigate these possibilities. Obviously, the types of sites available for CO and H_2 adsorption under reaction conditions may differ from those seen on fresh or used catalysts. In situ IR studies under reaction conditions could shed additional light on this subject. Such studies are also planned.

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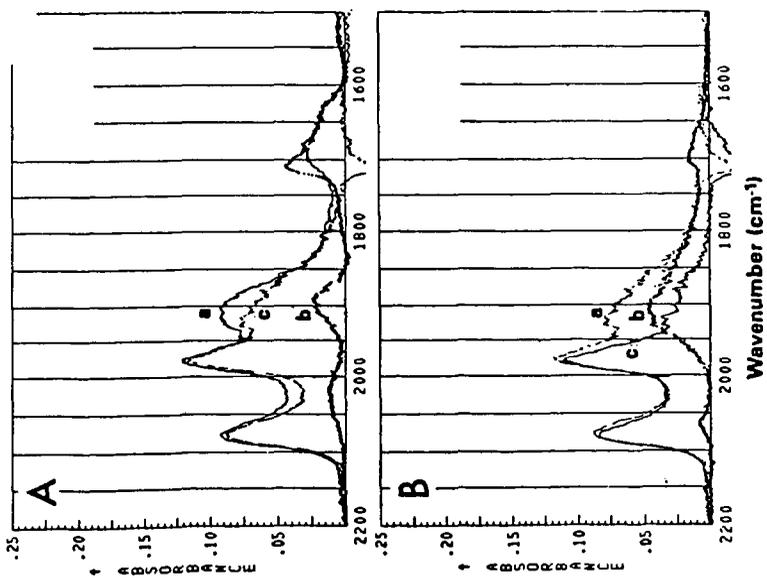


Figure 1. Spectra of CO adsorbed on SX Pd/Devison 57 silica (ex PdCl₂).
 A. Spectra showing "cooling" correction
 a) CO (2.3 Torr); b) μ_2 ; c) (a-b)
 B. Spectra showing strongly and weakly-held CO.
 a) "corrected" CO spectrum = C above
 b) CO held after 5 min. evac. c, (a-b) = weakly-held CO.

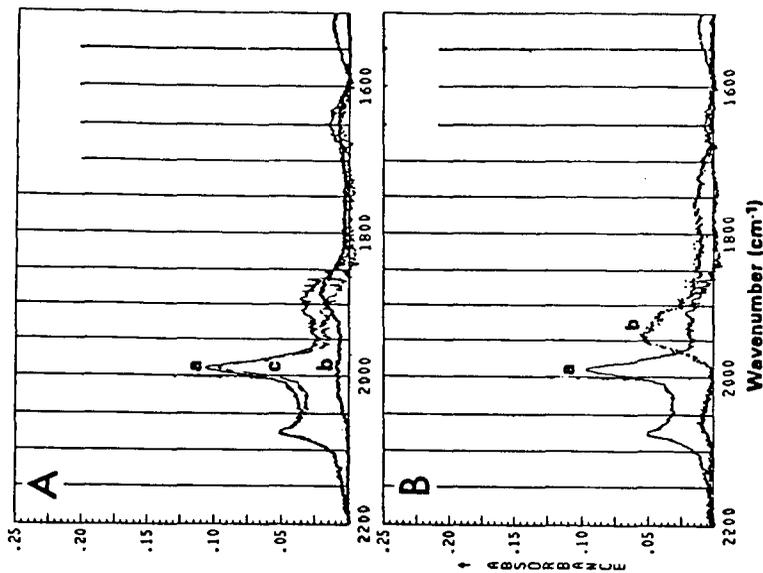


Figure 2. Spectra of CO adsorbed on SX Pd/Devison 59 silica (ex Pd(NO₃)₂).
 A. Spectra showing "cooling" correction
 a) CO (2.3 Torr); b) μ_2 ; c) (a-b)
 B. Spectra showing weakly and strongly-held CO
 a) weakly-held CO; b) strongly-held CO

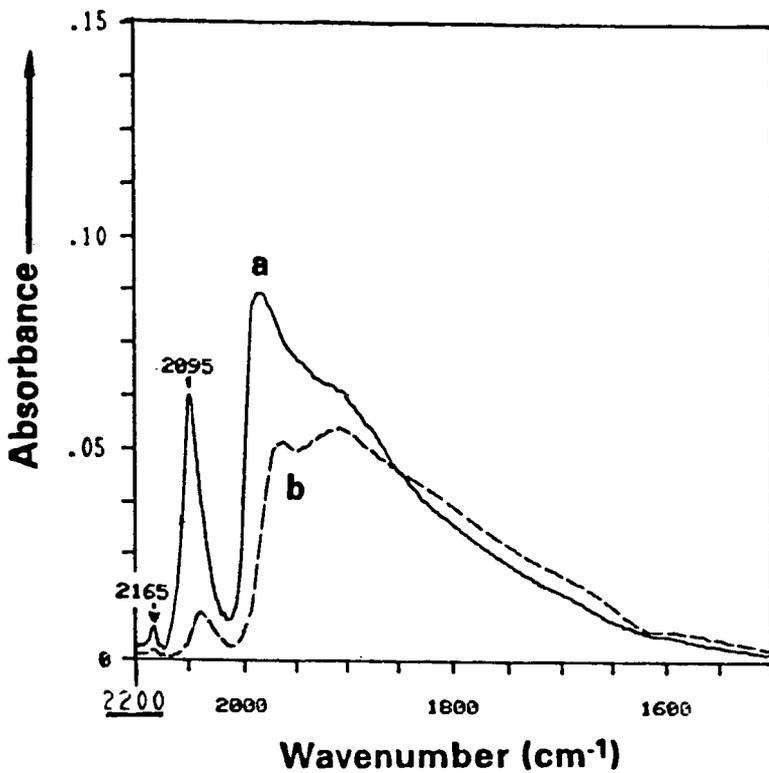


Figure 3. FTIR Spectrum of CO Adsorbed on 1.5% Pd/Davison 57 silica (ex PdCl₂)
 A. CO (2.0 Torr);
 B. After 5 min. evacuation.

(The background was subtracted, but no corrections were applied.)

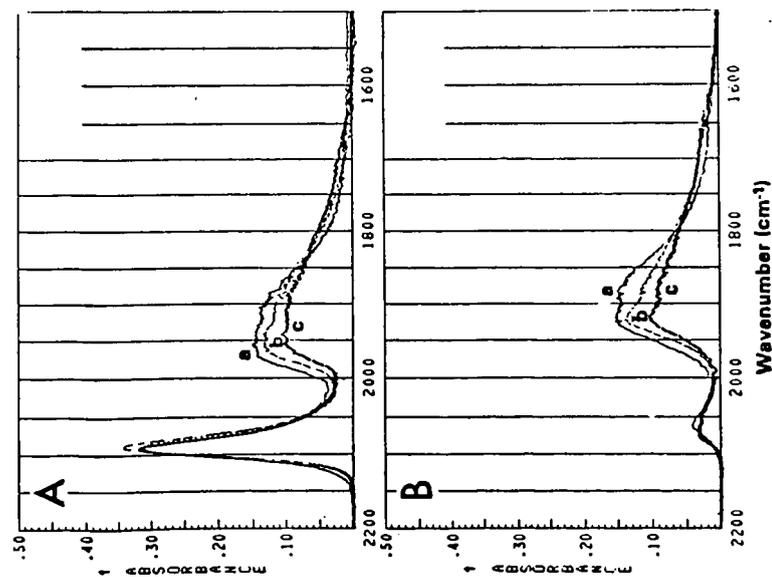


Figure 4, Effects of Li on 1.5% Pd/Devisium 59 silica (ion exchanged)
 A. Spectra of CO (2.1 Torr-corrected for "cooling") on catalysts containing the following Li contents:
 a) 0%; b) 0.7%; c) 1.02
 B. Spectra of CO retained after 5 min. evacuation on the same catalysts (a, b and c above).

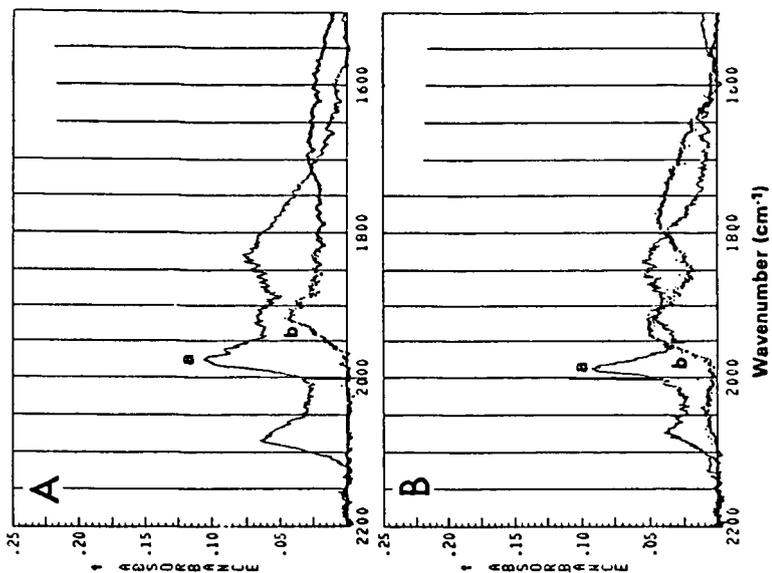


Figure 5, Effects of Li on 5% Pd/SiO₂
 A. CO/5% Pd/1.6% Li/SiO₂
 a) 0% CO (3.2 Torr-corrected); b) after 5 min. evacuation.
 B. CO/5% Pd/1.6% Li/SiO₂
 a) CO (2.1 Torr-corrected); b) after 5 min. evacuation.