

SSITKA Investigation of Palladium Precursor and Support Effects on CO Hydrogenation over Supported Pd Catalysts

S. H. Ali and J. G. Goodwin, Jr.¹

Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261

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CO hydrogenation on supported Pd catalysts was investigated using steady-state isotopic transient kinetic analysis (SSITKA) in order to explore the differences in catalytic behavior which have been previously reported by others to result from using different supports and Pd precursors. In this study, two different precursors [PdCl₂ and Pd(NO₃)₂] and three supports [SiO₂, Al₂O₃, and SiO₂-Al₂O₃] were investigated. The dispersion of the Pd particles on the prepared catalysts, as evaluated by CO chemisorption, was not affected by either the Pd precursor or the support used. In addition, for a given support the catalysts exhibited almost the same selectivities during CO hydrogenation toward methane, methanol [MeOH], and dimethyl ether [DME]. However, catalysts prepared using PdCl₂ showed higher overall activities than those prepared using Pd(NO₃)₂ for a given support. The nature of the support altered significantly the activity and the selectivity of the Pd. The order of activities at steady-state for a given precursor was Al₂O₃ > SiO₂-Al₂O₃ > SiO₂. The activity of the Pd/SiO₂-Al₂O₃ was lower than expected probably due to the relatively high level of S (500 ppm) present in the support as an impurity. It was found that Pd/SiO₂ produced essentially only MeOH. The use of acidic supports [Al₂O₃ and SiO₂-Al₂O₃] resulted in the formation of DME due to the secondary reaction of MeOH on acid sites of the supports. DME production was found to be limited by the amount of MeOH formed. Pd on the acidic supports also produced significant amounts of methane. SSITKA results showed [after considering readorption effects] that the Pd precursor used, or more specifically its anion [Cl⁻ and NO₃⁻], had a slight effect on the *intrinsic activity* of the sites producing methane ($1/\tau_{\text{methane}}$) [Cl⁻ > NO₃⁻] and a significant effect on the *surface coverage* of the intermediates leading to methane (N_{methane}) [Cl⁻ > NO₃⁻]. On the other hand, the precursor used had little or no effect on the *intrinsic activity* of the sites producing MeOH ($1/\tau_{\text{MeOH}}$) or the *surface coverage* of MeOH intermediates (N_{MeOH}). The nature of the support altered only slightly the *intrinsic activities* of the sites producing methane and MeOH. However, the number of *surface intermediates* leading to methane and MeOH were significantly affected by the support used and were in the order Al₂O₃ > SiO₂-Al₂O₃ and Al₂O₃ > SiO₂-Al₂O₃ > SiO₂, respectively. It is, thus, the effect of the support on the concentration of active sites/intermediates on Pd that

determines the impact of the support on the reaction rate. © 1998

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INTRODUCTION

Since the early study by Poutsma *et al.* (1) of CO hydrogenation on Pd, many investigations of this catalytic system have been reported. Supported Pd catalysts have been found to behave differently depending on the type of the support used (1–7). The interactions between Pd and the supports, suggested to cause these different behaviors, have been explained by a change in the electronic charge density at the Pd surface and a reduction in the capability of Pd to chemisorb CO. It has been reported that the acidity of the support used can alter the selectivity and/or the activity of the Pd for CO hydrogenation (8–10).

In addition to the support used, the type of the anions in the Pd precursor salt used in catalyst preparation may alter the reaction properties of the resulting catalyst. Deligianni *et al.* (11) and Kelly *et al.* (12) have studied the impact of chloride ions on the activity of supported Pd catalyst for methanol production, where the source of the chloride ions was the Pd precursor and not impurities in the support. Both studies showed that Pd precursors containing chloride ions resulted in an increase in the overall catalytic activity due to an increase in TOF.

Steady-state isotopic transient kinetic analysis (SSITKA) is one of the most powerful kinetic techniques for analyzing surface reactions. It permits the measurement of the concentration of surface intermediates and their intrinsic activities. Details about SSITKA have been presented in a recent review (13).

The purpose of this investigation was to study in detail, using SSITKA, the impact of various Pd precursors and supports on the surface residence times and concentrations of the intermediates leading to methane, methanol (MeOH), and dimethyl ether (DME) during CO hydrogenation reaction over various supported Pd catalysts. Such measurements taken under reaction conditions can help us

¹ To whom correspondence should be addressed.

to better understand the underlying causes of differences seen in catalytic behavior.

EXPERIMENTAL

Materials

The three different supports used were SiO₂ (Davison 952), γ -Al₂O₃ (Vista B), and SiO₂-Al₂O₃ (Davison 135). The surface areas and pore volumes were as follows: SiO₂, 219 m²/g and 0.51 cc/g; γ -Al₂O₃, 299 m²/g and 1.69 cc/g; SiO₂-Al₂O₃, 475 m²/g and 0.77 cc/g. Two Pd precursors were used to prepare the catalysts: palladium(II) chloride (Aldrich) and palladium(II) nitrate (Johnson Matthey).

Catalyst Nomenclature

Each one of the six catalysts prepared is designated by six letters. The first two letters are Pd, which refers to the active metal used to prepare all the catalysts used in this investigation. The third and the fourth letters are either Cl or NO, which reflects the type of the precursor used (Cl for the chloride precursor, and NO for the nitrate precursor). The last two letters are either Si (SiO₂), Al (γ -Al₂O₃), or SA (SiO₂-Al₂O₃) for the support used.

Catalyst Preparation

All the catalysts which were used in this study were prepared in the same manner in 10 g batches. The first step was the impregnation of a support by the incipient wetness technique using an aqueous solution of one of the two Pd precursors in order to produce a final reduced catalyst with 5 wt% Pd. After that, the prepared catalyst was dried in an oven for 12 h at 115°C, calcined at 400°C for 5 h in air (Praxair, 99.999% pure), and reduced at the same temperature using H₂ (Praxair, 99.999% pure) after purging with He. Both the calcination and the reduction procedures were performed using a gas stream having a flow rate of 60 cc/min and a temperature ramp rate of 1°C/min. Finally, after purging the reduced catalyst with He, it was passivated at room temperature for 2 h using 2% O₂/He (Praxair, 99.999% pure).

Elemental Analysis

ICP was used to determine the concentrations of the major impurities in the supports used and the loading of Pd in the various prepared catalysts. This analysis was performed by Galbraith Laboratories, Inc.

CO Chemisorption

Each of the catalysts was re-reduced in flow before chemisorption according to the reduction procedure given above in the catalyst preparation section. H₂ was then evacuated from the cell at 400°C for 1 h. The temperature was

then decreased to room temperature. After introducing CO to the cell containing the catalyst, the total and the reversible isotherms were evaluated according to the method reported by Kazi *et al.* (14). By taking the difference between the total and the reversible chemisorbed CO, the number of exposed Pd metal atoms could be calculated by assuming that CO_{irrev}/Pd_s = 1. The average particle size of Pd (d_p) was calculated using the following equation:

$$d_p \text{ (nm)} = \frac{5[\text{wt fraction of Pd(g Pd/g cat)}][\text{conversion factor}(10^7 \text{ nm/cm}^3)]}{[\text{CO}_{\text{irrev}}(\text{mol/g cat})][N_{\text{Avo}}(\text{atom/mol})][S_{\text{APd}}(\text{nm}^2/\text{atom})][\rho_{\text{Pd}}(\text{g Pd/cm}^3)]}$$

It is important to note that the calculated average particle size of supported Pd catalysts based on this method has been found to be in very good agreement with the values obtained using TEM (14).

Standard Reaction and Steady-State Isotopic Transient Kinetic Analysis (SSITKA)

A quartz microreactor was loaded with 0.05 g of a calcined/reduced/passivated catalyst sample. After re-reduction of the catalyst at 400°C, the reaction of CO (Praxair, 99.999% pure) and H₂ (Praxair, 99.999% pure) was started at 220°C and 1.8 atm. The reactants were further purified using a Matheson 450 Purifier filled with 4 Å molecular sieve (for CO) and an Alltech Gas Purifier packed with Drierite and 5 Å molecular sieve (for H₂). No oxygen trap was used for the H₂ due to its ultrahigh purity. A ratio of H₂/CO = 8 was used to minimize deactivation. After 3 min of reaction, the first sample of the effluent was analyzed by a gas chromatograph (Varian 3700 GC) equipped with a 6 foot, 60–80 mesh Porapak-Q column, and a flame ionization detector (FID). Steady-state reaction was reached during 24 h on stream.

Isotopic transients were taken by switching (using a pneumatic valve operated electronically) from ¹²CO (Praxair, 99.999% pure) to ¹³CO (Isotech, 99.999% pure) after 24 h of reaction. A Leybold-Inficon Auditor-2 mass spectrometer (MS) with a high-speed data acquisition system was used to detect the amounts of different isotopically labeled species. Constant pressure was maintained for the two reactant streams being switched by the use of two back-pressure regulators. Ar was present in a small concentration in the ¹²CO in order to permit determination of gas phase holdup. The concentration of Ar (5% of the ¹²CO stream) was not sufficient to perturb the reaction stationary-state during the switch from (¹²CO + Ar) to ¹³CO.

RESULTS

Elemental Analysis

Table 1 shows the results of ICP analysis for support impurities and Pd. All the prepared catalysts were confirmed

TABLE 1
Catalyst Composition

Catalyst	Pd (wt%)	Support	Impurity composition (ppm)						
			IA	IIA	Ti	Fe	Al	P	S
PdCl/Si	5	SiO ₂	570 Na 160 K	150 Mg 750 Ca	120	96	220	83	30
PdNO/Si	5	"							
PdCl/Al	5	Al ₂ O ₃	300 Na	5 Mg	5	50	N.A.	—	—
PdNO/Al	5	"							
PdCl/SA	5	SiO ₂ -Al ₂ O ₃	—	700 Ca	—	300	N.A.	—	500
PdNO/SA	5	"							

to have a weight percentage of Pd equal to 5 wt% as expected because of the method of preparation used (incipient wetness). All the catalysts had significant levels of impurities. This will be discussed later.

CO Chemisorption

The Pd dispersions and the average Pd particle sizes of the supported Pd catalysts were calculated and are reported in Table 2. The Pd dispersions were essentially the same (within experimental error) for all the catalysts prepared ($17 \pm 2\%$). The average Pd particle sizes of the catalysts were in the range 4.9–6.5 nm.

CO Hydrogenation

Rates and selectivities. Table 3 shows the results for CO hydrogenation on the differently supported Pd catalysts under both initial and steady-state reaction conditions. The initial rates were determined after 3 min of reaction in order to achieve gradientless conditions in terms of temperature and reactant concentration. The steady-state rates were after 24 h of reaction. The highest CO conversion under the conditions used was less than 2%, which meant that differential reaction conditions could be assumed. No evidence of mass or heat transfer limitations was detected for any of the

reaction experiments as evidenced by the activation energies determined for the formation of methane. In addition, the highest CO conversion to MeOH was much less than equilibrium conversion of CO to MeOH for the conditions used (<20% of approach to equilibrium).

Figure 1 shows the time-on-stream behavior for the rate of CO conversion on the various catalysts. The overall rates for CO conversion on the various catalysts went through maximum values, then stabilized as time proceeded. Similar initial induction periods have been noted for this reaction on Pd catalysts previously (15–17). The time corresponding to the maximum value of the overall rate of CO conversion varied between 30 and 300 min. For a fixed type of Pd precursor, the catalysts supported on Al₂O₃ had the highest overall rates of CO conversion, while the catalysts supported on SiO₂ had the lowest (except for the initial rate where PdNO/SA had the lowest value). In addition, the overall rates of CO conversion were somewhat higher for catalysts prepared using the PdCl₂ precursor than those using Pd(NO₃)₂ for a given support, especially in the cases of Al₂O₃ and SiO₂-Al₂O₃.

Figure 2 shows the time-on-stream behavior for the rate of conversion of CO to methane on the various catalysts. As time proceeded, the rate of formation of methane decreased for all the Pd catalysts. The Pd/Al₂O₃ catalysts had the

TABLE 2
Characteristics of the Catalysts

Catalyst	Pd wt% ^a	Total chemisorbed CO ^b (μmol/g cat)	Reversibly chemisorbed CO ^b (μmol/g cat)	% Pd dispersion ^c	Average particle size of Pd crystallites ^c (nm)
PdCl/Si	5	92	12	17	5.5
PdNO/Si	5	95	13	17	5.4
PdCl/Al	5	105	15	19	4.9
PdNO/Al	5	104	16	19	5.0
PdCl/SA	5	80	11	15	6.4
PdNO/SA	5	81	13	15	6.5

^a From ICP. Maximum error = $\pm 5\%$.

^b Maximum error = $\pm 5\%$.

^c Calculated based on irreversible CO chemisorption.

TABLE 3
CO Hydrogenation Results^a

Catalyst	% CO conversion ^b		Rate of CO conversion ^b ($\mu\text{mol/g cat/s}$)		TOF _{CO} ^c (10^{-3} s^{-1})		% Selectivity ^d			
	Initial ^f	S-S ^g	Initial ^f	S-S ^g	Initial ^f	S-S ^g	Methane		Oxygenates ^e	
							Initial ^f	S-S ^g	Initial ^f	S-S ^g
PdCl/Si	0.12	0.13	0.07	0.07	0.8	0.9	3	1	97	99
PdNO/Si	0.10	0.11	0.06	0.06	0.7	0.7	4	2	96	98
PdCl/Al	0.98	0.85	0.53	0.46	5.9	3.9	69	33	31	67
PdNO/Al	0.79	0.57	0.43	0.31	4.9	3.5	69	19	31	81
PdCl/SA	0.17	0.39	0.09	0.21	1.3	3.0	97	27	3	73
PdNO/SA	0.07	0.24	0.04	0.13	0.6	1.9	96	18	4	82

^a Reaction conditions: 220°C, 1.8 atm, H₂/CO = 8.

^b Maximum estimated error = $\pm 5\%$.

^c TOF calculated by dividing rate by CO_{irrev}.

^d Carbon selectivity.

^e MeOH + DME.

^f Initial results taken at 3 min of reaction.

^g Steady-state results taken at 24 h of reaction.

highest activities for methane formation, while the Pd/SiO₂ catalysts had the lowest activities (ca. 2 orders of magnitude less than Pd/Al₂O₃). However, initially the selectivity for methane was highest for Pd/SiO₂-Al₂O₃ (ca. 97%) and lowest for Pd/SiO₂ (ca. 4%). At steady-state, all the catalysts had methane selectivities lower than 33%, with that of Pd/SiO₂ $\leq 2\%$.

Since DME is formed from MeOH (produced on Pd sites) in a secondary reaction on acid sites (see Ref. (21) for more details), MeOH and DME need to be considered together when discussing the synthesis of MeOH on the Pd sites. The time-on-stream behaviors for the rate of CO conversion to oxygenates [MeOH and DME] (Fig. 3) show that

the production of oxygenates tended to follow the same trend as that for the overall rate. This increase in the rate of formation of oxygenates during the induction period is the focus of another paper (15). This increase was not due just to the conversion of sites producing methane to ones producing MeOH since the rate of CO hydrogenation increased overall. The same effects of Pd precursor and support on the relative rates of formation of the oxygenates at steady-state were observed as found for overall CO reaction. This is not surprising since at steady-state all the catalysts had oxygenate selectivities between 67 and 99%. Table 3 shows that the highest initial selectivities for

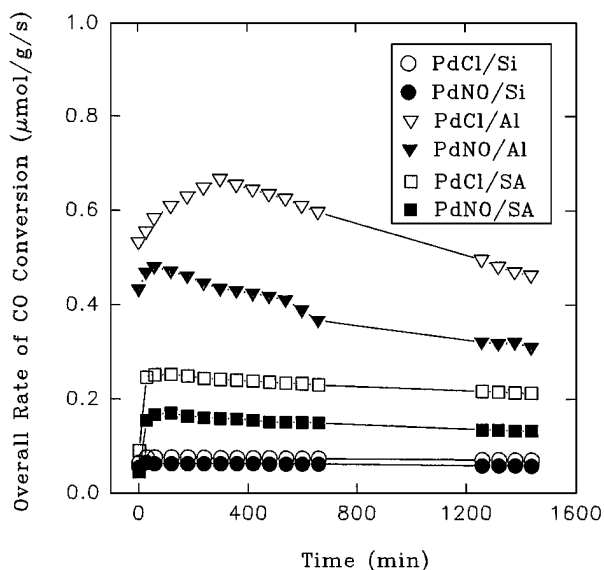


FIG. 1. Overall rate of CO conversion vs time-on-stream.

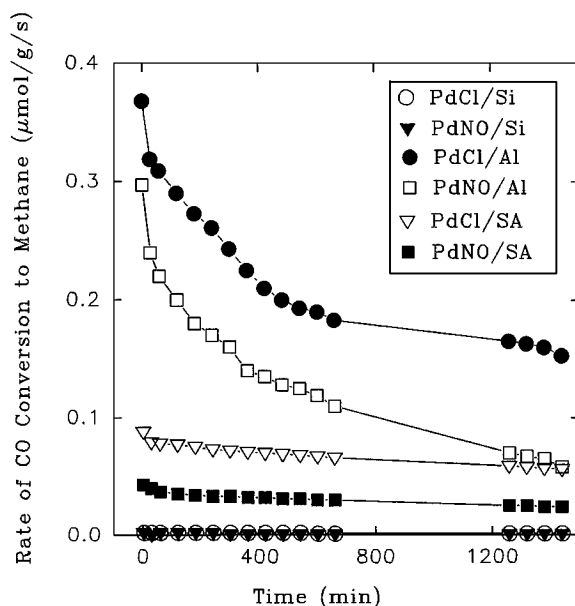


FIG. 2. Rate of CO conversion to methane vs time-on-stream.

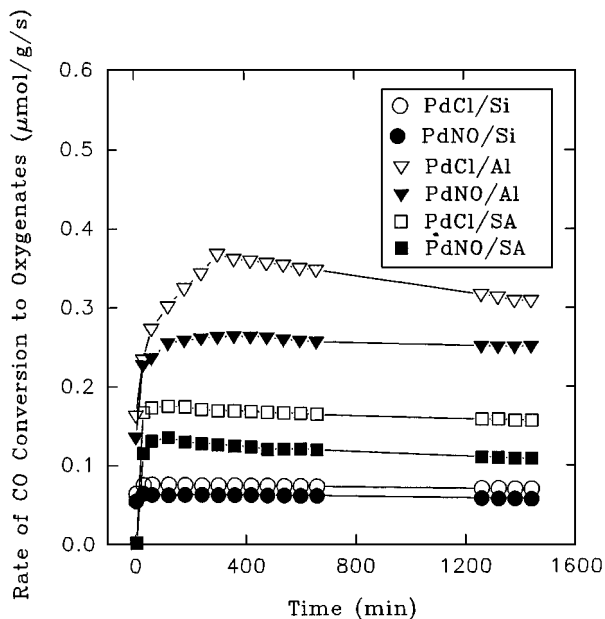


FIG. 3. Rate of CO conversion to oxygenates (MeOH and DME) vs time-on-stream.

oxygenate production were for the catalysts supported on SiO_2 (ca. 97%), while the catalysts supported on $\text{SiO}_2\text{-Al}_2\text{O}_3$ had the lowest (ca. 4%). Pd/SiO_2 exhibited at all conditions the highest oxygenate selectivities (ca. 96–99%).

Since DME is produced by secondary reaction of MeOH, it is obvious that the trend observed for oxygenates production (MeOH + DME) with respect to time-on-stream (Fig. 3) also is seen for DME production (Fig. 4). The catalysts supported on SiO_2 were not able to produce DME

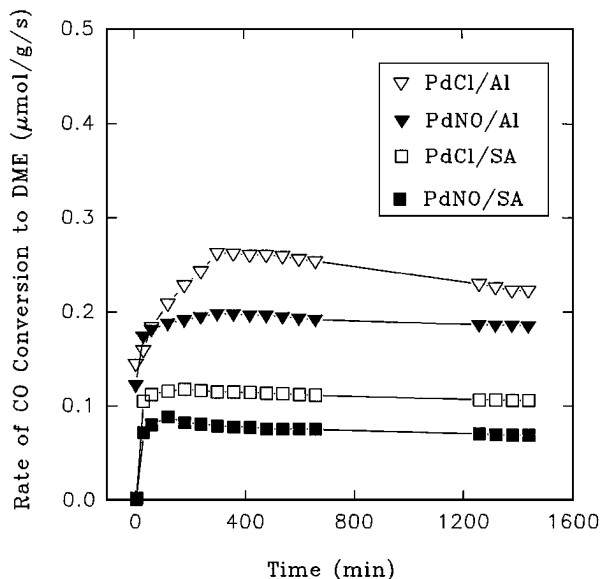


FIG. 4. Rate of CO conversion to DME vs time-on-stream.

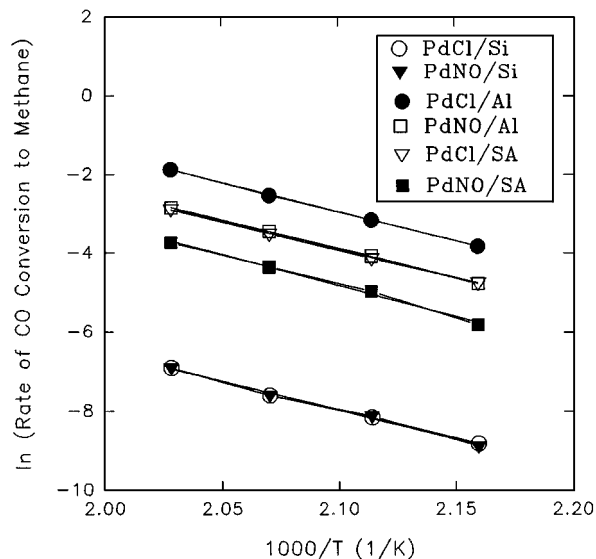


FIG. 5. Arrhenius plot of the rate of CO conversion to methane.

from MeOH due to the lack of acid sites of sufficient strength on the SiO_2 . This has also been clearly shown by separate experiments in which blank SiO_2 was added to the Pd/SiO_2 catalyst bed (21).

The Arrhenius plots for the formation of methane and the oxygenates (MeOH and DME) are shown in Figs. 5 and 6. These figures indicate that the apparent activation energies in the temperature range 190–220°C did not vary significantly upon varying the Pd precursor or the nature of the support. The apparent activation energies of formation of methane and oxygenates were found to be ca. 120 and 70 kJ/mol, respectively, for all the catalysts, similar to values reported in the literature for supported Pd catalysts (2, 6, 8, 18–20).

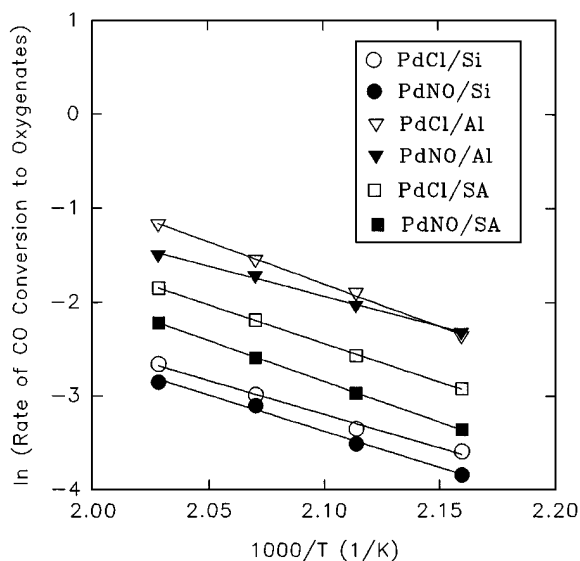


FIG. 6. Arrhenius plot of the rate of CO conversion to oxygenates.

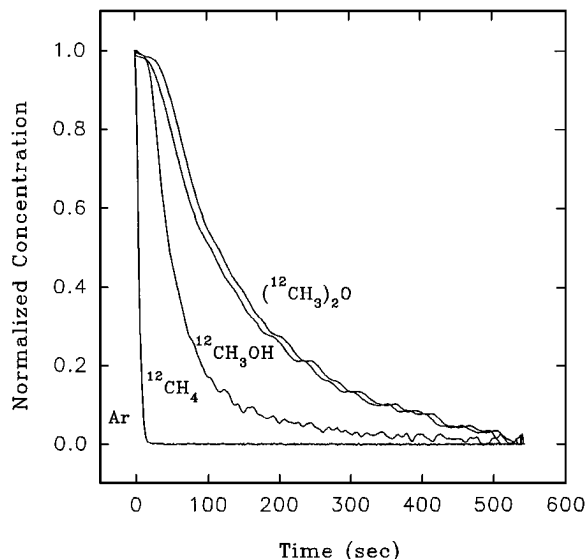


FIG. 7. Typical set of steady-state isotopic transients of Ar, $^{12}\text{CH}_4$, $^{12}\text{CH}_3\text{OH}$, and $(^{12}\text{CH}_3)_2\text{O}$ following a $^{12}\text{CO} + \text{Ar}/^{13}\text{CO}$ switch [for PdNO/Al at 220°C].

SSITKA measurements. Figure 7 shows a typical set of normalized isotopic/inert transients following the step replacement of ^{12}CO by ^{13}CO during SSITKA for PdNO/Al at steady-state reaction. The values of the average surface residence times of the species of interest (τ_i) were obtained by determining the area between the curves of these species and the one corresponding to the inert tracer Ar. Table 4 summarizes the SSITKA results for CO hydrogenation over the various supported Pd catalysts used in this investigation at steady-state (at 24 h of reaction) in terms of the average surface residence times for the C-containing surface intermediates leading to either methane, MeOH, or DME (τ_{methane} , τ_{MeOH} , or τ_{DME}).

τ_{methane} could not be determined for either PdCl/Si or PdNO/Si because of their low activities for methane

formation. The values of both τ_{methane} and τ_{DME} (see Table 4) had higher values for the catalysts supported on $\text{SiO}_2\text{-Al}_2\text{O}_3$ than on Al_2O_3 . The values of τ_{MeOH} were in the order $\text{Pd/SiO}_2\text{-Al}_2\text{O}_3 > \text{Pd/SiO}_2 > \text{Pd/Al}_2\text{O}_3$ for a given Pd precursor. τ_i 's for Pd on a given support prepared from Pd nitrate were greater than those (for the same species) on the catalyst prepared from Pd chloride. Since DME is produced by a secondary reaction from MeOH, τ_{DME} is always greater than τ_{MeOH} , as was found to be the case here. τ_{DME} is, thus, the sum of τ_{MeOH} [representing the average surface residence time of MeOH intermediates on the Pd sites] and the average residence time of the intermediates on the acid sites producing DME [τ_{acid}] (see Ref. (21) for details). τ_{acid} can be estimated using the following equation:

$$\tau_{\text{acid}} = \tau_{\text{DME}} - \tau_{\text{MeOH}}$$

Table 4 contains the values of τ_{acid} calculated for Pd/Al $_2$ O $_3$ and Pd/SiO $_2$ -Al $_2$ O $_3$.

DISCUSSION

Impact of Pd Precursor

To focus on the effect of the type of Pd precursor on the catalyst properties, we will compare catalysts which have the same support. The type of Pd precursor had no apparent impact on Pd dispersion. In addition, the Pd precursor had little significant impact on the behavior of the supported Pd relating to the presence of an induction period and the way the catalysts deactivated after that period. However, the total rate of CO conversion was somewhat higher for the catalysts prepared using PdCl $_2$ rather than Pd(NO $_3$) $_2$ precursor at steady-state, with a maximum difference of as much as 160% for methane and 35% for oxygenates. Deligianni *et al.* (11) found that Pd/SiO $_2$ catalysts prepared by either impregnation or ion exchange methods using a PdCl $_2$ precursor had 25% more activity for MeOH

TABLE 4

Reaction and SSITKA Results for CO Hydrogenation at Steady-State^a

Catalyst	Rate of CO conversion to specific products ^b ($\mu\text{mol/g cat/s}$)			τ_i (s)			τ_{acid} (s)
	Methane	MeOH	DME	Methane ^c	MeOH ^d	DME ^d	$\tau_{\text{Acid}} = \tau_{\text{DME}} - \tau_{\text{MeOH}}$
PdCl/Si	0.001	0.07	0	—	126	0	—
PdNO/Si	0.001	0.06	0	—	148	0	—
PdCl/Al	0.153	0.09	0.22	55	115	131	16
PdNO/Al	0.058	0.07	0.19	69	141	151	10
PdCl/SA	0.056	0.05	0.10	72	132	165	33
PdNO/SA	0.024	0.04	0.07	83	154	179	25

^a Reaction conditions: 220°C , 1.8 atm, $\text{H}_2/\text{CO} = 8$, at 24 h of reaction.

^b Maximum estimated error = $\pm 5\%$.

^c Maximum estimated error = ± 2 s.

^d Maximum estimated error = ± 3 s.

synthesis than ones prepared using either $\text{Pd}(\text{NO}_3)_2$ or $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$. Kelly *et al.* (12) concluded that the chloride ions contained in the Pd precursor increased the activity of MeOH formation over Pd/SiO₂ by virtue of increasing the TOF. Thus, the results obtained in this investigation with respect to the impact of the Pd precursor are in good agreement with the literature with regards to overall rate ($\text{Cl}^- > \text{NO}_3^-$) (11, 12). In addition, for the SiO₂-Al₂O₃ and Al₂O₃ supported catalysts, the selectivity to oxygenates at steady-state was somewhat greater for the catalysts prepared using Pd(NO₃)₂. However, for Pd/SiO₂, the type of the Pd precursor had no impact on the selectivities of the products (methane, MeOH, and/or DME).

The rates of formation of DME were higher for catalysts prepared using the PdCl₂ precursor than Pd(NO₃)₂ for a given acidic support. However, the rate of DME formation appears to have been primarily determined by the amount of MeOH produced in the system. This can be easily seen in Fig. 8 where the rate of CO conversion to DME is plotted versus the total P_{MeOH} (total P_{MeOH} is taken to be the partial pressure of MeOH exiting the reactor in addition to the equivalent partial pressure of the MeOH which was converted to DME). Figure 8 shows clearly the linear dependency of the rate of formation of DME on the amount of MeOH available in the gas phase. In addition, from Table 4 it can be determined that the fraction of the MeOH originally produced which was converted to DME was not affected by the type of the Pd precursor. It was in the range of 0.71–0.73 for Pd/Al₂O₃ and 0.67–0.64 for Pd/SiO₂-Al₂O₃. Thus, one can conclude that the rate of DME formation was determined primarily by the gas phase concentration of MeOH (which was limited).

Usually, the intrinsic activity is estimated by dividing the rate of formation of a product by the number of exposed surface metal atoms determined by chemisorption (TOF). However, this requires the strong assumption that the number of sites is equal (or at least proportional) to the number of surface metal atoms. A more accurate way to estimate the intrinsic activity of the active sites (true TOF) is by the inverse of the average surface residence time of the species under consideration obtained by SSITKA. This inverse of the particular average surface residence time, $k_i = 1/\tau_i$, is a pseudo-first-order rate constant, having units of TOF (13). One is cautioned to remember, however, that k_i for CO hydrogenation (to either methane or MeOH) is also dependent on the surface hydrogen concentration (N_{H}) due to the fact that the rate-limiting step involves hydrogen (22).

The calculated values of k_i given in Table 5 show only a small effect of the different Pd precursors on the activities of the Pd sites producing methane and MeOH ($\text{Cl}^- > \text{NO}_3^-$). On the other hand, the pseudo-first-order intrinsic activities of the acid sites leading to the formation of DME (evaluated from $1/\tau_{\text{acid}}$) appear to have been significantly higher when Pd(NO₃)₂ was used rather than PdCl₂. However, as discussed below, these differences also can be concluded not to be significant.

The accuracy of the average surface residence times of the particular products obtained by SSITKA can be affected by readsorption. Readsorption has been found to be a function of the partial pressure and the flow rate for MeOH and DME (15, 21, 22). Readsorption causes an overestimation of the surface residence times of these species on the active sites.

Due to the lack of any significant readsorption of methane, τ_{methane} and consequently k_{methane} are accurate reflections of the activities of these catalysts for methane formation. Thus, it would appear that the use of PdCl₂ resulted in methane synthesis sites slightly more active than when Pd(NO₃)₂ was used. The influence of the anions (Cl^- and NO_3^-) in the Pd precursors used on CO hydrogenation has to have been an indirect one since they were removed to a large extent during the pretreatment procedure used (reduction). However, it has been found previously that the impact of Cl⁻ modification of Ru/SiO₂ on CO hydrogenation remains even though the chlorine atoms are removed by H₂O formed during reaction (23).

Due to the fact that CO hydrogenation was performed over the various catalysts in this investigation at the same flow rate (space time), the impact of interparticle readsorption on the values obtained for τ_{MeOH} for the various catalysts can be assumed to be approximately the same. Nevertheless, readsorption in the pores of the various catalysts during CO hydrogenation over the various supported Pd catalysts may have caused some variation in the values of τ_{MeOH} because of the different P_{MeOH} 's produced by the

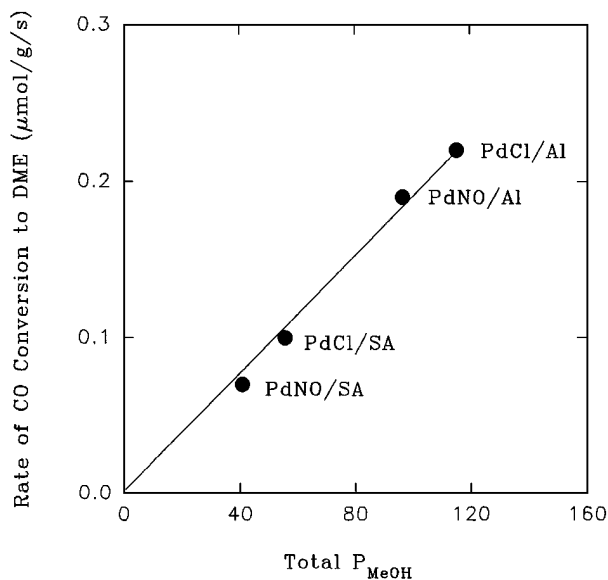


FIG. 8. Rate of CO conversion to DME vs total equivalent P_{MeOH} [total $P_{\text{MeOH}} = P_{\text{MeOH}} + (2P_{\text{DME}})$].

TABLE 5
Product Partial Pressures and Intrinsic Activities at Steady-State^a

Catalyst	P_{MeOH} (Pa)	P_{DME} (Pa)	Pseudo-first-order intrinsic activities (10^{-3} s^{-1})		
			$k_{\text{methane}} = 1/\tau_{\text{methane}}^b$	$k_{\text{MeOH}} = 1/\tau_{\text{MeOH}}^c$	$k_{\text{acid}} = 1/\tau_{\text{acid}}^d$
PdCl/Si	26	0	—	7.9	—
PdNO/Si	22	0	—	6.8	—
PdCl/Al	33	41	18.2	8.7	62.5
PdNO/Al	26	35	14.5	7.1	100.0
PdCl/SA	19	19	13.9	7.6	30.3
PdNO/SA	15	13	12.0	6.5	40.0

^a Reaction conditions: 220°C, 1.8 atm, $\text{H}_2/\text{CO} = 8$, at 24 h of reaction.

^b Maximum estimated error = $\pm 7 \times 10^{-3} \text{ s}^{-1}$.

^c Maximum estimated error = $\pm 0.2 \times 10^{-3} \text{ s}^{-1}$.

^d Maximum estimated error = $\pm 20 \times 10^{-3} \text{ s}^{-1}$.

different activities. This means that, where P_{MeOH} 's were higher due to higher rates of MeOH formation, the values of τ_{MeOH} obtained were closer to the accurate reaction site residence times of the active MeOH intermediates because of more competition for readsorption (21). The comparison between the various catalysts for their intrinsic activities for MeOH formation can, thus, only be a relative one. Because of the differences in P_{MeOH} resulting from using different Pd precursors, the slight relatively higher values of k_{MeOH} for catalysts produced using PdCl_2 rather than $\text{Pd}(\text{NO}_3)_2$ can be assumed to be negligible. Thus, the results of this investigation would seem to indicate that the type of the Pd precursor had little or no effect on the intrinsic site activity for MeOH formation. This is, thus, contrary to the suggestion of Deglianni *et al.* (11) that Pd/SiO₂ catalysts prepared from PdCl_2 have higher MeOH synthesis activities than those prepared from non-chlorine-containing precursors due to higher TOF's. Probably, this difference in conclusions is due to the difference in estimating site activity using an indirect (TOF based on chemisorption) versus a more direct ($1/\tau_{\text{MeOH}}$) method.

As suggested earlier in this section, differences seen in τ_{acid} and k_{acid} may actually not be significant. Larger variations in these parameters may result due to the fact that τ_{acid} is calculated by the difference between two experimentally measured values (τ_{DME} and τ_{MeOH}) each affected by readsorption. Thus, no conclusions about possible precursor effects on the acid sites can be made at this time.

Table 6 contains the values of the surface concentration of intermediates leading to methane, MeOH, and DME (N_{methane} , N_{MeOH} , N_{acid}). Note that N_{DME} is not used due to the fact that the intermediates at any time giving rise to DME consist of MeOH intermediates on Pd sites and (MeOH \rightarrow DME) intermediates on acid sites. The surface concentration of methane was calculated according to the following equation (13):

$$N_{\text{methane}} = R_{\text{methane}} \tau_{\text{methane}}.$$

In order to accurately account for all the intermediates leading to MeOH on Pd active sites, N_{MeOH} was calculated using the following equation (21):

$$\begin{aligned} N_{\text{MeOH}} &= R_{\text{MeOH}} \tau_{\text{MeOH}} + R_{\text{DME}} \tau_{\text{MeOH}} \\ &= R_{\text{Oxygenates}} \tau_{\text{MeOH}}, \end{aligned}$$

where all rates are in terms of molecules of CO reacted. N_{acid} , representing the number of surface intermediates leading to DME on the acid sites of the catalysts, was determined by the following equation (21):

$$N_{\text{acid}} = 0.5 R_{\text{DME}} \tau_{\text{acid}}.$$

The factor 0.5 is used because R_{DME} is in terms of CO converted but DME contains 2 carbons.

Because of the known weak ability of methane for readsorption after its production, the reported values for N_{methane} in Table 6 represent accurate values for the number of surface intermediates leading to methane. Thus, the results in Table 5 clearly show that using PdCl_2 instead of

TABLE 6
Surface Concentration of the Active Reaction Intermediates at Steady-State^a

Catalyst	N_i ($\mu\text{mol/g cat}$)		
	Methane ^b	MeOH ^c	Acid ^d
PdCl/Si	—	8.8	0
PdNO/Si	—	8.9	0
PdCl/Al	8.4	35.7	1.8
PdNO/Al	4.0	36.7	1.0
PdCl/SA	4.0	19.8	1.7
PdNO/SA	2.0	16.9	0.9

^a Reaction conditions: 220°C, 1.8 atm, $\text{H}_2/\text{CO} = 8$, at 24 h of reaction.

^b Maximum estimated error = $\pm 0.7 \mu\text{mol/g cat}$.

^c Maximum estimated error = $\pm 2.7 \mu\text{mol/g cat}$.

^d Maximum estimated error = $\pm 0.4 \mu\text{mol/g cat}$.

$\text{Pd}(\text{NO}_3)_2$ gave a significantly larger number of surface intermediates/sites leading to methane.

Although the surface concentration of intermediates of a particular species i (N_i) is the most accurate parameter obtained by SSITKA since its calculation is based simply on a mass balance, its meaning can be altered as a result of readsorption (15, 21, 22). Even with readsorption, however, N_i still reflects the number of surface molecules which gave rise to the product. Since readsorption may take place on inactive sites as well as on active ones, N_i may overestimate the number of active intermediates producing that species. MeOH is known to readily readsorb (15, 21, 22). However, it would appear that the type of the Pd precursor had little (if any) impact on N_{MeOH} (see Table 6). The differences in N_{acid} , on the other hand, are probably not significant due to errors introduced during the calculation of τ_{acid} , as mentioned earlier.

In summary, one can conclude that, while use of the PdCl_2 precursor resulted in significantly higher CO hydrogenation rates for Al_2O_3 - and SiO_2 - Al_2O_3 -supported Pd, the higher rates were mostly due to higher concentrations of surface intermediates for methane (related to the number of methane-producing sites) and the high selectivity for methane formation. The higher rates were not due to any significant differences in intrinsic site activity. Pd/SiO_2 did not exhibit any significant effect from the use of the PdCl_2 precursor apparently because of its low methane selectivity.

Impact of the Support

The nature of the support was found in this investigation to alter the catalyst activity and selectivity toward CO hydrogenation. This is similar to the findings of others (8–10, 24). Ryndin *et al.* (8), based on a study of Pd on seven different supports (SiO_2 , Al_2O_3 , La_2O_3 , ZrO_2 , ZnO , MgO , and TiO_2), concluded that the type of the support used greatly affects the reactivity of Pd for the production of MeOH and hydrocarbons. In this investigation it was found that Pd/SiO_2 had a MeOH selectivity of almost 99% similar to what has been found by others [including (8, 9)]. On the other hand, $\text{Pd}/\text{Al}_2\text{O}_3$ in this investigation had somewhat lower oxygenate selectivity compared to other reported studies [including (8, 9)]. Many investigators have found that the acidity of the support alters the activity of Pd for CO hydrogenation (8–10, 24).

The results in Table 5 show that the nature of the support had little significant effect on the pseudo-first-order intrinsic activity of the sites producing methane and, especially, MeOH as evidenced by the small changes in the values of k_{methane} and k_{MeOH} upon changing the support for a given type of Pd precursor. However, due to the potential errors in the estimation of the pseudo-first-order intrinsic activity of the sites producing DME, no conclusions will be made as to effects of the acid supports on k_{acid} .

The results given in Table 6 show that using Al_2O_3 instead of SiO_2 - Al_2O_3 resulted in a significant increase in the surface concentration of species leading to methane. The results in Table 6 also show that N_{MeOH} was significantly affected by the nature of the support ($\text{Al}_2\text{O}_3 > \text{SiO}_2$ - $\text{Al}_2\text{O}_3 > \text{SiO}_2$) even though Pd dispersion was similar.

There have been a number of hypotheses as to the possible mechanism(s) of the support effect on CO hydrogenation on Pd and other metals. They can be summarized as follows:

- (a) promotion/poisoning by impurities in the support (31);
- (b) support acidity (9, 24);
- (c) assisting sites (especially the concentration of -OH groups) on the support (26 and references in 27);
- (d) metal-support interactions leading to different Pd surface structures (7);
- (e) metal-support interactions leading to the stabilization of $\text{Pd}^{\delta+}$ sites (27); and
- (f) decoration/promotion of the metal surface by support species (31).

Several of these hypothetical mechanisms potentially overlap. While the latter four hypothetical effects cannot be addressed on the basis of the results of this investigation, the effect of impurities and support acidity can be.

Although in a study of Pd supported on three different silicas Kelly *et al.* (12) concluded that impurities were not responsible for the differences seen in their MeOH synthesis activities, it is well known that Cl (12), certain group IA (9, 12, 14, 22, 26), group IIA (5, 27), and Fe (28) atoms have an important promotion effect on CO hydrogenation on Pd. Many of these atoms are typically present as impurities in support materials, as is the case here (see Table 1). Cl has been discussed under the section on the impact of the Pd precursor. It most likely was present in the catalysts prepared from PdCl_2 , although elemental analysis for Cl was not performed in this study after catalyst preparation. However, most residual Cl present after catalyst preparation was probably removed during CO hydrogenation (23).

The SiO_2 and Al_2O_3 supports used contained Na (570 and 300 ppm, respectively). SiO_2 also contained a small amount of K (160 ppm). Pitchon *et al.* (26) and Kikuzono *et al.* (9) have reported that the effect of alkali species on MeOH synthesis on Pd varies in the order

$$\text{Li} > \text{Na, unpromoted} > \text{K} > \text{Rb} > \text{Cs} = 0.$$

Alkali promotion usually requires high levels of the promoter (>0.1 wt%) in order to see any significant effect (9, 12, 14, 22, 26). Thus, it would appear that the presence of Na impurities and very small amounts of K would not have much of an effect.

SiO_2 and SiO_2 - Al_2O_3 contained 700–750 ppm of Ca, while SiO_2 also contained 150 ppm of Mg. Although group

IIA elements have been shown to affect CO hydrogenation on Pd (5, 27), we expect that the levels present in this study are also too low to have a detectable effect.

Fe was present in all the supports at levels from 50 to 300 ppm. Fe promotion has been shown to increase the rate of CO hydrogenation on Pd (28); but it is unlikely, on the basis of the results in Ref. (28), that levels <0.02 wt% would have much of an impact. Likewise, there is no evidence to suggest that the low levels of Ti and P present would have any significant effect on the Pd.

The only impurity that probably had an effect was the S in the $\text{SiO}_2\text{-Al}_2\text{O}_3$ (at a level of 500 ppm). It is known that levels greater than 100 ppm in the support can have a detrimental effect on the activity of supported Co Fischer-Tropsch catalysts (29, 30). The impact of S on the activity of the Pd/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst is addressed further just below.

While there has been much discussion about the possible role of the formation of formyl species on the support in the overall rate of MeOH synthesis (31), one thing is clear from the literature: activity of supported Pd increases with support acidity (9, 24). In this study, the order of overall activity of the catalysts was $\text{Al}_2\text{O}_3 > \text{SiO}_2\text{-Al}_2\text{O}_3 > \text{SiO}_2$. Thus, compared to the earlier findings (9, 24), it would appear that Pd/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ was much less active than expected. This lower activity is consistent with the presence of the high levels of S in the $\text{SiO}_2\text{-Al}_2\text{O}_3$ support.

Salvador and Kladnig (25) found that MeOH reacts on HY zeolite to produce DME and concluded that this is related to the Brønsted acidity of the zeolite. Thus, it is not surprising that acid sites on the support of a supported Pd catalyst would be able to convert primary product MeOH to DME. In this investigation, the catalysts supported on SiO_2 did not produce any DME due to the lack of acidic sites of sufficient strength. On the other hand, the nature of the acidic supports ($\text{SiO}_2\text{-Al}_2\text{O}_3$ and Al_2O_3) did not appear to have any major effect on N_{acid} . This, however, was probably due to a lack of saturation of the acid sites as a result of the low partial pressures of MeOH. Thus, more cannot really be said about the acid sites and their formation of DME since they were underutilized.

CONCLUSIONS

Neither the Pd precursor nor the support had a major impact on the initial dispersion which was in the range of 15–19% for all the catalysts prepared. While this dispersion may have changed during reaction, the conclusions based on the initial reaction results are essentially the same as those based on the steady-state reaction ones. All catalysts exhibited induction periods during which the overall CO hydrogenation rates increased significantly. Steady-state rates were similar to initial rates except in the case of the Pd/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts which had steady-state rates 2–3 times greater than the initial rates.

For a given support, while the type of the Pd precursor used did not have a major effect on the selectivities of the products (especially for Pd/ SiO_2), the rates of the formation of these products were always greater for the catalysts prepared from PdCl₂ than from Pd(NO₃)₂. Using PdCl₂ precursors resulted in slightly higher methane synthesis site/intermediate activities (as determined by SSITKA) than using Pd(NO₃)₂. On the other hand, after considering readsorption effects on the evaluated SSITKA parameters, it is suggested that the Pd precursor had little or no effect on the activity of MeOH synthesis sites. Because of the way that τ_{acid} was calculated (by the difference between two experimentally measured values, τ_{DME} and τ_{MeOH}) and the probable lack of acid site saturation, no conclusions can be made about any possible effect of the anions contained in the Pd precursors on the intrinsic activities and the surface concentrations of the acid sites of the supports producing DME. Using PdCl₂ instead of Pd(NO₃)₂ resulted in a significant increase in the number of intermediates/sites leading to methane. On the other hand, the type of the Pd precursor had little or no impact on the surface coverage of the intermediates leading to MeOH. It is concluded that the Cl-containing precursor's main effect was on the number of intermediates/sites producing methane.

Even though the nature of the support was not found to alter the catalyst dispersion, it did alter both the catalyst activity and selectivity for CO hydrogenation. DME was found to be formed only on acidic supports such as Al_2O_3 and $\text{SiO}_2\text{-Al}_2\text{O}_3$. It was found that the rate of formation of DME was constrained by the limited available concentration of MeOH in the gas phase. The "true" intrinsic activities (evaluated from $1/\tau_i$, and after considering readsorption) of the Pd sites forming methane and MeOH were found to be only slightly affected by the nature of the support. However, the SSITKA results show clearly that the nature of the support altered significantly the number of intermediates/sites producing methane ($\text{Al}_2\text{O}_3 > \text{SiO}_2\text{-Al}_2\text{O}_3$) and MeOH ($\text{Al}_2\text{O}_3 > \text{SiO}_2\text{-Al}_2\text{O}_3 > \text{SiO}_2$). The relatively lower activity of the Pd/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ is suggested to be due to the high level (500 ppm) of S present as an impurity in the support. Other impurities in the supports are suggested to have had little effect on the catalysts. Due to the probable lack of saturation by DME precursors of the acid sites, no conclusions could be made concerning the differences between the acid sites on Al_2O_3 and those on $\text{SiO}_2\text{-Al}_2\text{O}_3$.

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