On the Selectivity of Palladium Catalysts in Synthesis Gas Reactions

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Reactions of CO/H_2 mixtures have been studied on a series of Pd/SiO_2 catalysts (2 wt% Pd) with and without a promoting additive. Mg and La compounds were used as promoters. It appeared that promoters (i) influence the activity of the catalysts and (ii) increase the selectivity for "oxygenates" and suppress the selectivity for CH_4. The activity for methanol synthesis is linearly correlated with the amount of Pd extractable from the reduced and used catalysts as Pd–acetylacetonate. Since it is known that promoters also create a new type of ionic adsorption center for CO and NO adsorption, it is concluded that Pd "ions" are indeed the centers for activation of CO toward methanol whereas Pd metal supplies hydrogen atoms for hydrogenation.

INTRODUCTION

For reasons which are well known, reactions of synthesis gas (CO/H_2) have attracted much attention in recent years (1). Because of the relatively high price of synthesis gas production, only reactions leading to highly valuable products are of practical interest. Among these reactions those producing oxygen-containing compounds ("oxygenates") are the most promising ones.

The simplest compound among the various oxygenates which can be formed from CO/H_2 is methanol. Good "metallic" catalysts for methanol synthesis have been known for a long time (2, 3). They are based on Cu and combinations of various oxides (ZnO, Al_2O_3, Cr_2O_3, etc.). Also Fe (4–6) and Fe/Rh alloys (7) are known as catalysts producing oxygenates as well as hydrocarbons. Nevertheless, it was quite surprising when Poutsma *et al.* (8) reported that methanol can also be produced, and with high selectivity, by palladium catalysts. Since in contrast with the earlier mentioned catalysts (4–7), Pd catalysts produce almost purely CH_3OH and CH_4, with no higher homologues of either, they

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seemed to be a very convenient subject for a study on one of the basic problems of selectivity in synthesis gas reactions, namely, the question as to which properties of the catalyst cause a metallic element (Pd (8) Rh (9–11), Ru (12), Pt (13)) to direct the CO/H_2 reaction toward oxygenates instead of to hydrocarbons.

Ichikawa (11) pointed out that Pd is a good catalyst for CH_3OH synthesis, but only when a suitable carrier is used. Later studies (14, 15) confirmed that conclusion. It has been shown that the best promoters of the catalytic properties of Pd are supports like MgO, La_2O_3, or Nd_2O_3. Behavior of Pd–Ag alloys, as well as some literature data on Pd, indicates (14, 16) that a considerable part of the CH_4 produced by Pd catalysts (e.g., Pd/Nd_2O_3) probably stems from oxygenated intermediates. On the basis of these and some other facts a suggestion has been put forward (14) that dispersed atoms and ions of Pd might be essential for catalysis of the essential steps in methanol synthesis (14) rather than bulk Pd metal. To gain more information on this tentative conclusion, the investigations reported in this paper have been performed. A series of Pd/SiO_2 catalysts have been prepared with a constant Pd/SiO_2 ratio (2 wt%) and a varying amount of magnesium-based promoters (Mg/Pd varied from 0.1 to 2.7). The cata-

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lysts were analyzed chemically and the content of extractable, i.e., formally ionic, Pd was determined. In parallel with this, the catalytic selectivity and activity were tested in CO/H_2 reactions, at 1 atm total pressure. Similar catalysts were also investigated by ir spectroscopy. Results of the first two studies are presented below; a short preliminary report on the ir spectra has already appeared (17).

EXPERIMENTAL

Apparatus

A conventional continuous flow, fixed-bed apparatus has been used for all the catalytic measurements. All experiments were performed at 1 atm total pressure, with the H_2/CO ratio of $\frac{2}{1}$. All measurements reported in this paper were made at a standard temperature of 488 ± 2 K. In a standard experiment, the flow was kept constant at the value of 0.6 liters/h. Before reaction, all catalysts were reduced at 573 K, for at least 18 h, with a hydrogen flow of 1.2 liters/h. After reduction, the catalyst was brought to the reaction temperature and hydrogen was replaced by the reaction mixture. Usually after about 24 h a steady state selectivity behavior was reached (reported in the subsequent tables and figures). After a further period of time, the activity of the catalyst started to decay. Analysis of products was performed by gas chromatography (Packard GLC 419) with a column filled with Porapak Q (4 m long, ϕ = 3 mm). Nitrogen (flow 1.8 liters/h) was used as a carrier gas, detection was by FID, and the column temperature was 310 K. Conversion of CO into CH_3OH at 1 atm pressure is limited to low values by the thermodynamics of the system; at 488 K a rough estimate shows that the maximum conversion into methanol is about 0.3% (18). However, values much lower than that can be easily analyzed by GLC.

Data Evaluation

GLC signals were converted into values proportional to the molar concentrations ("corrected" signals) by calibration factors determined experimentally (a repeated dilution procedure). Corrected signals were used to calculate the conversion α, defined as

$$\alpha = \frac{X}{N} \cdot 100\%,$$

where X = moles CO converted, and N = moles CO in the feed. Thus conversion of CO into hydrocarbons, methanol, and ether was considered in X; N was calculated from the macroscopic feed data. The selectivity for methanol production, $S(CH_3OH)$, is defined as

$$S(CH_3OH) = \frac{Y}{X} \cdot 100\%,$$

where Y = moles CH_3OH. With some catalysts a high $(CH_3)_2O$ production was observed. Since $(CH_3)_2O$ is evidently the product of a consecutive reaction, selectivity for "oxygenates" $S(OX)$ was evaluated as:

$$S(OX) = \frac{Y + 2[moles\ (CH_3)_2O]}{X} \cdot 100\%.$$

Catalyst Preparation

Series K. A solution of $PdCl_2$ in 0.1 N HCl was prepared and mixed with a solution of $Mg(NO_3)_2$, in the desired ratios. The resulting solution was brought into contact with SiO_2 (Kieselgel 60, Merck, Darmstadt, 0.2–0.5 mm, surface area ca. 400 m^2/g) and the liquid was removed by slow evaporation under stirring. The amount of $PdCl_2$ was such as to produce, after complete reduction, catalysts with a constant Pd/SiO_2 ratio of 2 wt%.

The content of Mg varied; the ratio MgO/SiO_2 was between zero and 4 wt%. The relevant Mg/Pd ratios are given in Table 1.

Because of the procedure applied, a part of the Mg was most likely present in the steady state catalyst as chloride. Nevertheless, for the sake of simplicity the additives are quantitatively characterized by "equiv-

TABLE 1

Composition and Particle Size (2r) of Catalysts

Additive, % MgO (wt%)	Code K	Mg/Pd atomic ratio	2r from XRD (nm)	$2r_{max}$ from TEM (nm)
—	K I	0	6	6
0.25	K II	0.33	8	—
0.35	K III	0.46	5	—
0.5	K IV	0.66	5	—
1.0	K V	1.33	4.5	—
2.0	K VI	2.65	5	—
3.0	K VII	3.98	4	—
4.0	K VIII	5.3	7	7[a]
Additive, % MgCl$_2$	Code L	Mg/Pd	2r from XRD (nm)	
0.2	L I	0.14	8.5	
0.5	L II	0.35	—	
2.0	L III	1.4	8.0	
5.0	L IV	3.5	8.0	
Additive, % MgO	Code M	Mg/Pd		
2.0	M	2.65		
Additive, % La$_2$O$_3$	Code N	La/Pd		
3.0	N I	1.0		
6.0	N II	2.0		
12.0	N III	4.0		
2% Pd/La$_2$O$_3$	N IV	—		

[a] Contains also some big particles (30–40 nm).

alents" of MgO,[2] and by the calculated Mg/Pd atomic ratios.

Series L. The same procedure as above was applied, except that MgCl$_2$ was used instead of the nitrate; the data are also shown in Table 1. For comparison, a chlorine-free catalyst (M) was prepared from Pd(NO$_3$)$_2$ and Mg(NO$_3$)$_2$ solutions; the Pd/Mg ratio of the catalyst was 0.4.

Series N. The same procedure as with series L was followed but for the N$_I$ and N$_{III}$ catalysts La$_2$O$_3$ was added as promoter dissolved in 1 N HCl and for N$_{II}$ in 1 N HNO$_3$.

Determination of the Extractable Pd

Koolstra (*19, 20*) has shown that when

[2] Scanning electron microscopic analysis revealed that on many spots Pd, Cl, and Mg are found together (see (*19*)).

Pd is deposited as PdCl$_2$ on the SiO$_2$ carrier, all of the Pd can be extracted under very mild conditions (within about 10%) from the carrier by acetylacetone. On the other hand, the data obtained with unpromoted Pd/SiO$_2$ indicate that Pd metal is most probably not removed by the same extraction procedure. Complexed, extracted Pd (most probably Pd(AcAc)$_2$) can be determined in the solution by X-ray fluorescence (using an Am 241 source and a Si–Li detector).

This analytical procedure (with a Dy secondary target) has been applied in this paper, and the amounts of extractable Pd (extractable under the given standard conditions and designated as Pd^{n+}) have been determined for the entire K series, and also for some other catalysts before and after their use in the reaction. Amounts of [Pd^{n+}] are experimentally determined in

counts per hour per 50 ml solution (the primary data output of the X-ray fluorescence analysis). An estimate was made of the amount of [Pd^{n+}] relative to the total amount of Pd present in the system ([Pd^{n+}] in % Pd_{total}) and these values are also shown below. It has to be remarked that for various reasons this gives the upper limit of the number of ions seen by the reaction mixture.

Extraction was performed in a simple cell, which allowed one to introduce oxygen-free AcAc to the catalyst. After reduction or after reaction, oxygen-free N_2 was blown through the AcAc reservoir in the upper part of the cell in order to remove dissolved oxygen. Then, under N_2, AcAc was brought into contact with the catalyst in the lower part. A closed reactor was then disconnected from the AcAc reservoir and the flow apparatus and placed into a flask-shaking machine. Extraction under continued shaking was performed overnight (about 16 h) at room temperature. After extraction the solution was filtered, its volume was determined and made up (with AcAc) to 50 ml total volume. This volume was analyzed by the X-ray fluorescence apparatus (Model Didac 800 from Intertech-
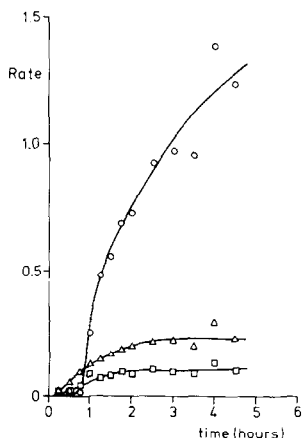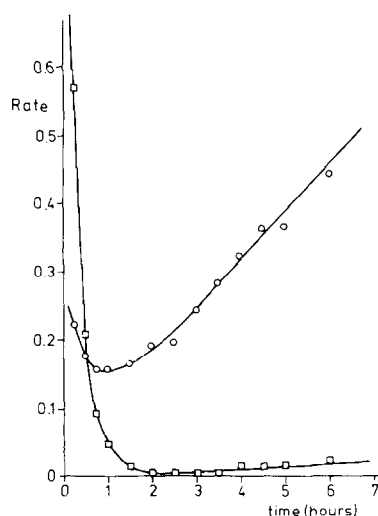
FIG. 2. Rate of reaction (expressed in 10^{-8} mole of the product in the flow) as a function of the time on the stream. M catalysts, 2.0% MgO. O, CH_3OH; □, CH_4.

nique with an Ortec 451 amplifier) in sealed plastic flasks of a standard form.

In general, analysis by X-ray fluorescence can be performed with a high accuracy. A main source of error here, however, is the possibly varying extractability of the Pd^{n+} present in various samples, and the adsorption of Pd(AcAc)$_2$ on the carrier and Pd metal. Similar errors accompany the calibration experiments with $PdCl_2/SiO_2$. No high accuracy is therefore claimed for the procedure applied, but it may be expected that the errors do not seriously influence the main characteristic features of the correlation between the activity and the amount of Pd^{n+} as presented below. The extractability of Pd^{n+} from La_2O_3-promoted catalysts is slightly lower than with pure SiO_2 catalysts.

RESULTS

When the flow of gases through the catalyst in the reactor was switched from pure H_2 to the reaction mixture ($CO/H_2 = \frac{1}{2}$), the activity and the selectivity of the catalyst both varied with time in a way which was typical for a given series of catalysts, as follows:

(i) with the series K and L catalysts (cata-

FIG. 1. Rate of reaction (expressed in 10^{-8} mole of the product in the flow) as a function of the time on the stream; typical results for catalysts of the K series (Table 1). O, CH_3OH; △, CH_3OCH_3; □, CH_4.

lysts with chlorine), methane and dimethyl ether were formed faster at first than methanol (Fig. 1);

(ii) with catalyst M (chlorine-free), only traces of dimethyl ether were formed, but also more methane than methanol was formed at the beginning of the reaction (Fig. 2), and this difference was more pronounced here than with the K and L catalysts, as is illustrated by Figs. 1 and 2.

Three variables are plotted in Fig. 3 as a function of the Mg/Pd ratio:

(a) concentration of Pd^{n+} in the catalyst after reduction, before use in the reaction;

(b) concentration of Pd^{n+} after reaction;

(c) catalytic activity in the pseudo-steady state at 488 ± 3 K.

A reasonably good correlation between the activity and the amounts of Pd^{n+} is immediately observable.

This correlation is better demonstrated in a graphical form, where activity is plotted as a function of the Pd^{n+} concentration. A correlation is found for both the K (i.e., Mg-promoted) and N (La-promoted) catalysts (Fig. 4). The selectivity $S(OX)$ is shown in Fig. 5.
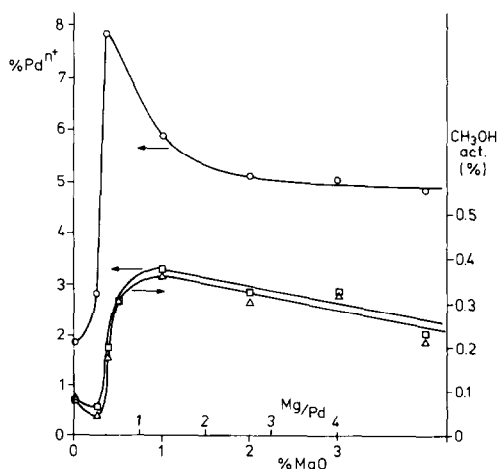

FIG. 4. Activity in CH_3OH formation at 488 K (defined as $\alpha \times S \times 10^{-2}$) as a function of the relative amounts of Pd^{n+}, extractable under given conditions from the K and M catalysts. $\square$, K series, Mg promoter; $\blacksquare$, M catalyst, Mg promoter; $\bigcirc$, La promoter; percentage of CO converted into all products; $\bullet$, La promoter; percentage of CO converted into methanol.

One can note that the $S(OX)$ and the activity curves have a similar shape when plotted as a function of the promoter concentration. Table 2 shows the selectivity behavior in more detail, in the form of product distributions.

It is obvious that the presence of Cl in the

FIG. 3. Left: relative amounts of extractable Pd^{n+} (under given conditions) from the catalysts of the K and M series (Table 1), before ($\bigcirc$) and after ($\square$) the reaction. Right: activity in CH_3OH formation at 488 K ($\alpha \times S \times 10^{-2}$, according to the definitions under Experimental) both as a function of Mg/Pd ratio (or MgO wt% relative to SiO_2).
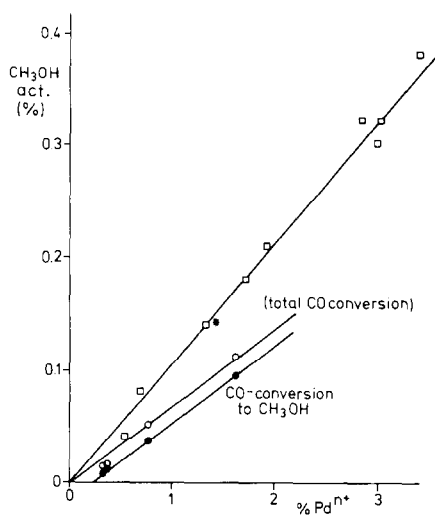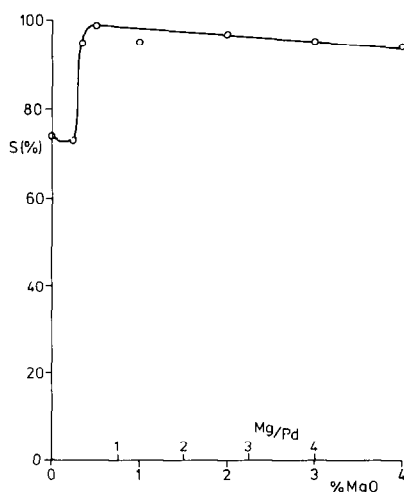

FIG. 5. Selectivity S (see Experimental) as a function of the Mg/Pd ratio, as in Fig. 3.

TABLE 2

Product Distribution from CO Hydrogenation Over
Pd and Pd-Promoted Catalysts ($T = 488$ K)

Catalyst	Product distribution (mole%)				$S(OX)^b$ (%)
	CH_4	CH_3OCH_3	CH_3OH	$\alpha_{CO}(\%)^a$	
K I	23	0.5	76	0.09	74
K II	27.5	1.5	71	0.04	73
K III	4	1	95	0.18	95
K IV	1	1	98	0.30	99
K V	6	7.5	86.5	0.38	95
K VI	3.5	6	90.5	0.29	97
K VII	5	9	86	0.34	95
K VIII	8	14.5	77.5	0.20	93
L II	10	10	80	0.13	92
L III	10	33	57	0.14	92
L IV	30.5	69.5	—	0.04	82
M	5.5	0.5	94	0.14	94
N I	43	2.5	54.5	0.02	58
N II	21.5	1	77.5	0.02	79
N III	27	12.5	60.5	0.05	76
N IV	4.5	—	95.5	0.11	95

[a] Measured after 24 h.
[b] CH_3OCH_3 included as $2(CH_3OH)$.

catalyst can lead to higher amounts of extractable Pd^{n+} ions and to the formation of higher amounts of dimethyl ether. However, the activity of the catalysts of the L series is lower than that of the K series catalysts.

When a pseudo-steady state activity was achieved, formation of CH_2O was also followed. The effluent gas was bubbled through 2 ml of a saturated solution of 2,4-dinitrophenylhydrazine in 2 N HCl. The 2,4-dinitrophenylhydrazine was then extracted by 2 ml of ethyl acetate and determined by gas chromatography (the procedure follows that described by Soukup *et al.* (*21*)). In this way the integral CH_2O formation over about 24 h was determined. Determination has been performed with two catalysts, namely, "2% MgO" from the K series, and the catalyst "3% La_2O_3" from the N series. The method does not allow more than a rough estimate of CH_2O formation and the results were as follows. With the K catalyst about $0.6 \times 10^{-4}\%$ carbon monoxide was converted into CH_2O; with the N catalyst the figure was 3 to 4 times higher. The analytical procedure did

not allow us to establish whether CH_2O is an intrinsic byproduct (a desorbing intermediate) of CH_3OH, or whether it is formed by a consecutive dehydrogenation of CH_3OH on the carrier or the metal.

DISCUSSION

The catalysts freshly reduced *in situ* and those in the pseudo-steady state clearly differ in their surface composition. This can be deduced from the behavior illustrated by Figs. 1 and 2.

These figures also demonstrate a difference in the behavior of chlorine-containing and chlorine-free catalysts. Such a difference has already been reported by other authors (*12, 22*). Figures 1 and 2 demonstrate that CO/H_2 or the oxygen-containing products (H_2O, CH_3OH) modify the catalyst, making it more active than the freshly reduced catalyst. The modification of the active centers, or their formation, cannot be a simple blocking action of one of the gases mentioned above; for instance, the activity toward CH_3OH production increases during the induction period and, in the case of Cl-containing catalysts, the CH_4 activity slowly increases also. An intentional carbon deposition by CO disproportionation, performed at 623 K after a standard reduction, only decreases the overall activity, and the catalysts with predeposited carbon initially produce pure methane, while the CH_3OH activity recovers only slowly and does not reach the maximum value possible (under standard conditions at the given temperature) (*23*). Therefore, we do not consider carbon deposition as a factor promoting the conversion into CH_3OH and as the factor responsible for the induction period in the CH_3OH formation.

Another possibility to be considered is that small particles of Pd^0 are modified and activated by the above mentioned gases, being converted into oxides or Pd–oxygen solution. However, bulk Pd oxide (as well as chloride) is rather unstable and when alone it is easily reduced by hydrogen or by the reaction mixture. Thus the most proba-

ble targets of the modification during the induction period are the Pd(II), Pd(I), or Pd^0 species dispersed (atomically?) in the matrix of the promoter or of the support.

This conclusion is closely related to the following point. It seems that data suggesting an answer to the question posed in the Introduction, namely which properties of the catalyst incorporating a metallic element like Pd cause the CO/H$_2$ reaction to be directed toward oxygenates instead of to hydrocarbons, are those of Fig. 4. We observe there that the activity of various systems is neatly correlated with the number of extractable Pd^{n+} ions. Of course, there is always a danger that this is not a causal but an incidental correlation: it is also the existence of the correlation which we would like to discuss, rather than its linear character and the absolute numbers of Pd^{n+} ions, etc. However, in our opinion, the following points indicate that Pd^{n+} species are indeed the centers for the CH$_3$OH formation:

(a) The CH$_3$OH synthesis is very sensitive to the choice of the carrier, while the Pd^0 particle size does not seem to play an essential role (14, 22, 24, 25). This is among others also the conclusion from Tables 1 and 2 of this paper.

(b) Carriers or promoters, which are known to form mixed oxides or chlorides (or oxy-chlorides) with Pd (26–29), are particularly suitable for making Pd catalysts active for CH$_3$OH synthesis. The obvious role of such carriers is to stabilize at close proximity the H atom producing centers (Pd^0) and the Pd^{n+} centers.

(c) It is known, and it is particularly remarkable, that various SiO$_2$ carriers, although of apparently the same chemical composition, lead to Pd catalysts of very different CH$_3$OH activity (see, e.g., Refs. (15, 24)). Also an admixture of Al$_2$O$_3$ into SiO$_2$ can modify the Pd activity favourably. This has led some authors to the conclusion that the acidity or basicity of the carriers is essential, either for the overall synthesis or for CH$_4$ formation (24, 30, 31). On the other hand, catalysts prepared from Na$_2$PdCl$_4$, or Pd supported on basic carriers like MgO, La$_2$O$_3$, or Nd$_2$O$_3$, are the best ones among the various Pd catalysts tested. Thus it seems that it is not the acid/base properties as such but the ability of a support to stabilize the active form of Pd that is essential. We suggest that this active form is palladium present as Pd^{n+} centers, bound to the carrier or to the promoter.

(d) Alloying the methane-producing metals (Ni, Ru, Co) with another metal of a low methanation activity (Cu) leads to a very dramatic decrease in the methanation activity (32–36). It has also been shown that this is caused by the fact that CO dissociation is an essential step in methanation and that it requires an ensemble of several active atoms to be present (32, 33). In contrast to this, alloying of Pd with Ag leads to surprisingly small effects, which are approximately of the order expected for the decrease in the number of Pd surface atoms caused by the alloying (14). This also indicates that CH$_3$OH formation is not a simple hydrogenation of CO on the Pd^0 particles and that not all CH$_4$ is necessarily formed in the same way, as for example, on Ni. The following picture makes the results with alloys (14) understandable:

(i) The Pd^0 metal surface is mainly active in supplying atomic hydrogen for hydrogenation of CO elsewhere, and the intrinsic methanation activity of this surface is low.

(ii) Most of the CH$_4$ formed on the Pd catalyst which is active in methanol synthesis originates from O-containing intermediates bound to other than Pd-metal sites. We suggest that these are the Pd^{n+} centers in the lattice of the promoter or carrier, as mentioned above.

(e) A parallel ir spectroscopic study on the Pd–methanol catalysts has revealed that promotion of Pd/SiO$_2$ by Mg or La compounds creates new adsorption sites for CO and NO (17). The ir frequencies of CO and NO adsorbed thereon indicate that the adsorbates are bound to positively charged Pd sites, as for example Pd^{1+} (37–40). The promoted (but not the pure) Pd/

SiO_2 catalysts revealed, after reduction, ESR signals which could be ascribed to Pd^{1+} ions, when the suggestions in the literature are followed (*38–40*).

The above-mentioned arguments (points a–e)) favor in our view the idea that a causal relation exists between the activity in methanol synthesis (the same catalyst produces methane at higher temperatures) and the number of Pd^{n+} species. Evidently, to keep these species unreduced, Pd has to be introduced into the system in a form of a mixed Pd compound: mixed chloride, oxide, oxychloride, surface silicate, etc. Active centers must also be in the nearest neighborhood of the Pd^0 clusters which supply hydrogen for hydrogenation. The activity is then obviously dependent on both the metallic surface area and the number of Pd^{n+} species.

We consider that the picture as described so far is consistently supported by the data presented in this paper as well as by the data in the literature. However, the data presented above leave some open questions which require further research. At the moment it is not possible to decide whether the induction period (see Figs. 1 and 2) is an additional reduction by CO (followed by, e.g., formation of carbonates) or, vice versa, the supplying of some oxygen by H_2O or CO which has been removed during the reduction by pure H_2. Ichikawa (*25*) reports that well-reduced active catalysts reveal an activated CO adsorption (at 200°C), and Bell (*22*) reports that active catalysts reveal defects (oxygen vacancies) which are responsible for an excessive O_2 adsorption. Such defects might be able to bind oxygen from CO or H_2O (*41*) Solymosi et al. (*42*) report that Rh on some carriers dissociates CO_2 much more easily than on others. This rather supports the second explanation suggested above. Let us mention here that preliminary experiments which we have performed with Cu/ZnO catalysts (prepared according to Herman et al. (*43*)) revealed that with these catalysts also there is an induction period observable in

CH_3OH synthesis, and that this period is shortened when an oxidized catalyst is used for reaction without a preceding reduction.

Another point which is not perfectly understood is why the curves in Figs. 3 and 5 go through a maximum. A possible reason is that a Mg/Pd compound which is present above the Mg/Pd ratio of about one is blocking the Pd^{n+} centers, preventing their catalytic action as well as their extraction.

Catalysts of the L series show a lower overall activity and a higher selectivity in ether formation. While the first phenomenon observed can be explained, for example, by the assumption that the $PdCl_2/MgCl_2$ combination is less well dispersed over the SiO_2 surface than the $PdCl_2/MgO$ combination, the second phenomenon is obviously related to the Lewis acidic properties of the mixed chlorides.

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