

# Promoting Effects of Lithium on Pd/CeO<sub>2</sub> Catalysts in Carbon Monoxide-Hydrogen Reactions

## Chemical Trapping and Temperature-Programmed Desorption Studies

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### ABSTRACT

At a low percentage, lithium (0.15%) increases the methanol activity and selectivity of a Pd/CeO<sub>2</sub> catalyst. Higher lithium loadings result in the appearance of ethanol (23.4% ethanol selectivity on 3% Pd-1% Li/CeO<sub>2</sub>) but with a decreased overall catalytic activity. The maximum amounts of surface formyl species and of adsorbed carbon monoxide correspond to the most active methanol synthesis catalyst (3% Pd-0.15% Li/CeO<sub>2</sub>). These results suggest that lithium can stabilize adsorbed carbon monoxide and surface formyl species. An increase in the temperature of desorption of carbon monoxide after carbon monoxide-hydrogen reaction (from 470 to 590 K) is attributed to an interaction between adsorbed CO and Li<sup>+</sup>. This interaction can both favour carbon monoxide dissociation and carbon monoxide insertion reactions. Temperature-programmed desorption after ethanol adsorption was performed and a mechanism of ethanol formation is proposed.

### INTRODUCTION

The following definition of promoters was given more than 70 years ago by Jobling [1]: "It has recently been discovered that there are other substances which, when added in minute quantity to a catalyst, increase its activity. Thus practically all metallic catalysts become activated when certain oxides or compounds or other metals are distributed throughout them". Nevertheless, nowadays, many aspects of the role of promoters are still unclear and even often the subject of controversy.

In carbon monoxide-hydrogen reactions, promoters are often used to enhance the productivity or selectivity with respect to olefins or oxygenated compounds. Thus, the addition of potassium to iron or ruthenium is known to increase the olefin selectivity [2]. An improvement in total activity and a shift in the selectivity towards longer chain hydrocarbons are observed after the addition of alkali metal compounds to iron catalysts [3]. On Ru/SiO<sub>2</sub>, a lower hydrogenation activity, as suggested by McClory and Gonzalez [4], is associ-

ated with site blockage by the alkali metal atom, resulting in a depressed activity. High methanol selectivity and activity have been reported by Kikuzono et al. [5] on catalysts prepared from  $M_2PdCl_4$  precursors ( $M$ =alkali metal).

In general on  $Pd/SiO_2$  catalysts, the improvement in the catalytic activity for methanol formation depends on the alkali metal cation in the decreasing order  $Li > Na \gg \text{unpromoted} > K$ . The caesium- and rubidium-promoted palladium catalysts did not produce methanol and had a low activity [5].

Different explanations for the influence of promoters in alcohol production systems have been proposed:

(i) The promoter maintains the active metal in a higher coordination. Thus good agreement between methanol formation and the palladium ion surface concentration has been reported by Poels et al. [6] and Driessen et al. [7]. Anikin et al. [8] have shown that a positive charge on palladium should favour the formation of surface formyl species, a possible intermediate of methanol. On rhodium-based catalysts, van der Lee et al. [9] could find no systematic correlation between  $C_2$  oxygenate formation and the amount of extractable metal ions, but such a correlation exists for methanol activity.

(ii) The promoter can stabilize one of the reaction intermediates. Hindermann et al. [10] established a clear relationship between methanol activity and surface formyl species. With formyl species the stabilization can be afforded by a positive charge on the metal, as shown by Anikin [8], or by the interaction of the oxygen end of the CO molecule with the promoter, as shown by Blyholder et al. [11] for the  $Fe-Li^+$  couple. In a recent paper, Diagne et al. [12] stated that formyl species seem to be the main intermediate in methanol synthesis on  $Pd/SiO_2$  and  $Pd/CeO_2$ .

(iii) The promoter can interact with one of the reagents during its adsorption. Thus on a potassium predosed  $Pd(100)$  surface, Berko and Solymosi [13] have shown that, on temperature-programmed desorption (TPD) of carbon monoxide, the peak temperature is shifted from 470 K (clean surface) to 619 K at a monolayer coverage [14]. They explained this increase in the desorption activation energy by an enhanced back-donation of metal d electrons into the lowest unoccupied molecular orbital,  $2\pi^*$ , of carbon monoxide. Angevaere et al. [15] observed only a slight influence on linear coordinated carbon monoxide in the promotion of  $Pd/SiO_2$  by potassium, but a new IR adsorption band appeared at  $1740\text{ cm}^{-1}$ . They concluded that this new band reflects a local  $CO-K^+$  interaction. Bands around  $1700\text{ cm}^{-1}$  have been observed by several workers on lanthana-, zirconia- and ceria-doped rhodium catalysts [16–18]. These bands were attributed to carbon monoxide coordinated to the metal by its carbon end and to the promoter by its oxygen end. The appearance of these species is not only restricted to the case where the promoters are deposited on the catalyst after its reduction [17,18].

(iv) Support acid sites can change the selectivity pattern by secondary re-

actions, e.g., alcohol dehydration to ethers and even to hydrocarbons [19]. Addition of alkali metals can neutralize these sites and thus alter the catalyst's properties [20,21].

(v) The promoter itself can form a catalytic centre, as shown on  $\text{MoO}_3$ -promoted  $\text{Rh/SiO}_2$  [22].

The purpose of this work was to study the influence of lithium added to  $\text{Pd/CeO}_2$ . Selectivity and activity were determined. Carbon monoxide adsorption properties and the stability of formyl species are discussed in terms of results acquired by TPD and chemical trapping techniques.

## EXPERIMENTAL

### *Catalyst preparation*

Cerium dioxide was precipitated from cerium nitrate (Fluka) by ammonia solution at pH 8, dried in air at 423 K (ca. 3 h) and calcined in air at 673 K (ca. 3 h).

Palladium catalysts were prepared by the conventional impregnation method with palladium chloride dissolved in 1 M hydrochloric acid, dried in air at 423 K (ca. 3 h) and calcined in air at 673 K (ca. 3 h).

Lithium was added as lithium hydroxide (Merck) during the impregnation and after cerium dioxide precipitation in the appropriate amounts.

### *Carbon monoxide chemisorption*

Pulses (0.87 ml) of pure carbon monoxide [N45 (Air Liquide), oxygen  $\leq 3$  ppm v/v, water  $\leq 3$  ppm v/v] were admitted on the catalysts at room temperature until no further chemisorption was observed. Carbon monoxide was determined by gas chromatography with thermal conductivity detection.

### *CO-2H<sub>2</sub> reaction*

The catalysts (500 mg) were reduced in hydrogen, the temperature being increased from room temperature to 573 K at  $1 \text{ K min}^{-1}$ , then maintained constant at 573 K for 12 h. After decreasing the temperature to 523 K, a carbon monoxide-hydrogen (1:2) flow of ( $2 \text{ l h}^{-1} \text{ g}_{\text{cat}}^{-1}$ ) was passed through the catalyst bed. All experiments were performed at atmospheric pressure.

### *Temperature-programmed desorption*

#### *After CO+2H<sub>2</sub> reaction*

The catalyst was exposed to a flow of carbon monoxide-hydrogen (1:2) ( $2 \text{ l h}^{-1} \text{ g}_{\text{cat}}^{-1}$ ) overnight under the same conditions as above and evacuated for a few hours at room temperature until all traces of products detected by gas

chromatography had completely disappeared (flame ionization detector for hydrocarbons and oxygenated compounds; Thermal conductivity detector for carbon monoxide and dioxide). HCHO, HCOOH, CH<sub>3</sub>COOH, H<sub>2</sub> and H<sub>2</sub>O were not followed.

#### *After ethanol adsorption*

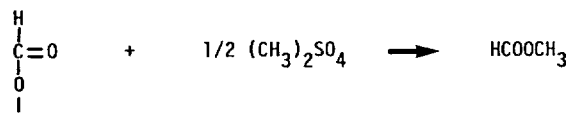
The catalysts were exposed to ethanol vapour (ca. 10 mmHg) under a flow of helium (2 l h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>) degassed at room temperature as described below.

The rate of temperature increase in the TPD studies was 6 K min<sup>-1</sup> (up to 800 K).

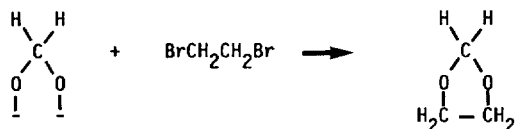
#### *Chemical trapping technique*

A surface intermediate adsorbed on the surface of the catalyst is contacted with an appropriate agent, giving rise to a compound which can be detected by gas chromatography with high sensitivity. A knowledge of the compound formed yields information on the adsorbed species. Many studies were performed in our laboratory in order to trap adsorbed species formed after carbon monoxide-hydrogen reaction:

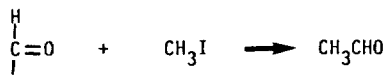
(i) Methyl formate can be formed if a methylating agent (e.g. dimethyl sulphate) is used, indicating the presence of formate species [23].



(ii) Dioxymethylenic species can be trapped as 1,3-dioxolane using dibromoethane [24]:



(iii) Formyl species can also be trapped as acetaldehyde or propanal, using methyl or ethyl iodide respectively, e.g.,



By mass spectrometry we established that on the rhodium catalyst (possibility of acetaldehyde formation starting from CO + 2H<sub>2</sub>), the percentage of deuterated acetaldehyde obtained after trapping with deuterated methyl iodide is higher than 70%. With a palladium catalyst, the chain growth is less impor-

tant. For this reason we conclude that the chemical trapping of the formyl species by methyl iodide is unambiguous.

### Apparatus

The glass reactor (Fig. 1) consists of three Rotaflow stopcocks (1, 2, 3), two fritted discs (4, 5) forming a compartment for the catalyst and, at the top of the reactor, a sampling compartment (8) closed at one end with a septum (7). Through the septum (6) it is possible to introduce different reactants and by closing stopcock (1) the sampling compartment is isolated from the remainder of the system.

### Procedure

The catalyst (0.5 g) was reduced by treatment with hydrogen ( $2 \text{ l h}^{-1} \text{ g}_{\text{cat}}^{-1}$ ) for 12 h at 573 K. The hydrogen was removed by evacuation at  $10^{-1}$  Torr (15 min). The compartment 8 was under vacuum during the reaction. Carbon monoxide was then introduced at 1 atm ( $1 \text{ atm} = 101.325 \text{ N m}^{-2}$ ) (523 K) for 30 min. The reaction was stopped rapidly with an excess of methyl iodide (1 ml, room temperature) introduced through the septum of stopcock 2, on the surface which was at the reaction temperature. Immediately stopcock 1 was opened and the system cooled (258 K). By closing stopcock 1, the gas was isolated from the catalyst, eliminating the problem of readsorption of acetaldehyde on the catalyst. Acetaldehyde was followed by gas chromatography (flame ionization detection) on Porapak Q at 403 K with nitrogen as the carrier gas). The experimental errors were, in this instance, within 15%.

Formate and methane are also detected after the chemical trapping. Methane is probably formed by reaction of hydrogen with the methyl group of methyl iodide. As is seen in the TPD experiments, the formates are probably located

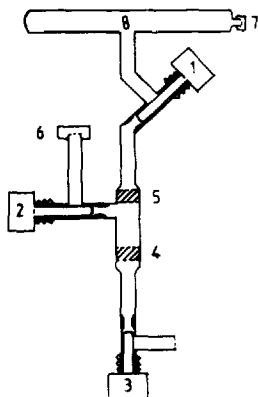


Fig. 1. Experimental apparatus for formyl trapping. 1-3, Rotaflow stopcocks; 4,5, fritted discs; 6,7, septa; 8, sampling compartment.

on the cerium dioxide support. Formyl species must be trapped under conditions where hydrogen is not present in the gas phase, as it is readily reduced to  $\text{CH}_3\text{O}$  species and can no longer be detected.

The other species proposed in our mechanism are not detected under the conditions of the present trapping experiments.

## RESULTS AND DISCUSSION

### *Carbon monoxide chemisorption*

Whereas a decrease in the active metal surface area due to blockage [25] might be expected on addition of lithium, Table 1 shows an increase in the metal surface area from 1.58 to 2.33  $\text{cm}^2 \text{g}_{\text{cat}}^{-1}$  for the undoped Pd/CeO<sub>2</sub> and the 0.15% Li-doped Pd/CeO<sub>2</sub>, respectively. Kelly et al. [26] found an increase in the metallic dispersion when 5% Pd/SiO<sub>2</sub> was promoted by Li<sub>2</sub>CO<sub>3</sub>, Li/Pd = 1 (31 and 62 for 5% Pd/SiO<sub>2</sub> and Li-doped Pd/SiO<sub>2</sub>, respectively). At higher lithium loadings ( $> 0.25\%$ ), a decrease in metallic area can be observed (Table 1). This is even more accentuated for 3% Pd-1% Li/CeO<sub>2</sub>, where the total carbon monoxide chemisorption is about 50% of the initial value ( $0.95 \cdot 10^{19}$  and  $2 \cdot 10^{19}$  molecules  $\text{g}_{\text{cat}}^{-1}$  for the doped and undoped samples, respectively).

### *CO + 2H<sub>2</sub> reaction*

As shown in Table 2, Pd/CeO<sub>2</sub> doped with 0.15% lithium (Catalyst II) has a better selectivity towards oxygenates (43.8%) than the unpromoted catalyst Ib (36.5%). The enhanced carbon monoxide chemisorption together with a better selectivity and activity with respect to oxygenates show that lithium not only increases the number of carbon monoxide chemisorption sites but also activates carbon monoxide towards the methanol synthesis. This enhanced

TABLE 1

Chemisorption of carbon monoxide on Pd-*x*% Li/CeO<sub>2</sub> at room temperature

Catalyst	Reduction temperature (K)	Molecules CO $\text{g}_{\text{cat}}^{-1} \times 10^{19}$	Surface area <sup>a</sup> ( $\text{m}^2 \text{g}_{\text{cat}}^{-1}$ )	Particle size (Å)	Dispersion
3% Pd/CeO <sub>2</sub> (Ia)	573	2.00	1.58	47.4	0.120
3% Pd-0.15% Li/CeO <sub>2</sub> (II)	573	2.96	2.33	32.1	0.174
3% Pd-0.25% Li/CeO <sub>2</sub> (III)	573	2.30	1.81	41.4	0.135
3% Pd-0.5% Li/CeO <sub>2</sub> (IV)	573	1.83	1.45	51.8	0.108
3% Pd-1% Li/CeO <sub>2</sub> (V)	573	0.95	0.75	100	0.056

<sup>a</sup> Assuming that  $n_s$  [number of surface atoms of Pd per unit area ( $\text{m}^2$ ) of polycrystalline surface] is  $1.27 \cdot 10^{19}$ .

TABLE 2

Carbon monoxide-hydrogen reaction at 523 K and 1 atm

Results were obtained after 12 h (stationary state).

Catalyst	Reduction temperature (K)	CO conversion <sup>a</sup>	CH <sub>4</sub>	C <sub>2+</sub> HC <sup>b</sup>	CH <sub>3</sub> OH	EtOH C <sub>2</sub> H <sub>5</sub> OH
3% Pd/CeO <sub>2</sub> (Ia)	573	0.22 <sup>c</sup>	9.0 <sup>c</sup>	—	91.0 <sup>c</sup>	—
3% Pd/CeO <sub>2</sub> (Ib)	573	0.059	59.7	3.7	36.5	Trace
3% Pd-0.15% Li/CeO <sub>2</sub> (II)	573	0.185	52.9	3.2	43.1	0.7
3% Pd-0.25% Li/CeO <sub>2</sub> (III)	573	0.163	64.0	10.2	17.5	8.0
3% Pd-0.5% Li/CeO <sub>2</sub> (IV)	573	0.171	67.3	11.8	12.9	8.0
3% Pd-1% Li/CeO <sub>2</sub> (V)	573	0.050	55.6	7.4	12.7	24.3

<sup>a</sup>Carbon monoxide conversion corresponds to the formation of methane, C<sub>2+</sub> hydrocarbons, methanol and ethanol (carbon dioxide is not included).

<sup>b</sup>HC = hydrocarbons.

<sup>c</sup>Results taken from ref. 12 (CO + 2H<sub>2</sub> reaction was carried out at 488 instead of 523 K).

methanol activity can be ascribed either to an interaction with the oxygen end of the CO molecule or to a decreased reducibility of the metal caused by the promoter [27].

At high lithium loadings (0.25 and 0.5%), an increase in C<sub>2+</sub> hydrocarbons is observed. The productivity in methane is only slightly altered but much more ethane appears. At the same time, a clear enhancement of C<sub>2</sub> oxygenates (essentially ethanol) occurs. This simultaneous increase in C<sub>2</sub> oxygenates and higher hydrocarbons suggest that a CH<sub>x</sub> surface intermediate could be involved in the formation of both hydrocarbons and oxygenates. Thus Favre et al. [28] observed that Pd/V<sub>2</sub>O<sub>3</sub> can produce C<sub>2</sub> oxygenates when external CH<sub>x</sub> groups are supplied by dichloromethane. Ethanol is also formed when dichloromethane is added to the synthesis gas on the unpromoted Pd/CeO<sub>2</sub> catalyst. It is therefore likely that the role of lithium in ethanol formation is to increase the concentration of surface CH<sub>x</sub> species. A decreased hydrogenation ability can explain this result. Indeed, the rate of hydrogenation of the CH<sub>x</sub> species to methane would decrease and as a consequence the probability of CH<sub>x</sub> polymerization (to give hydrocarbons) or to insert carbon monoxide (to produce C<sub>2</sub> oxygenates) would increase.

At a higher lithium loading (1%), an important decrease in the total carbon monoxide conversion is observed. An enhanced selectivity of ethanol is the consequence of the substantial decrease in hydrocarbon activity. It can be assumed here that, with an increased percentage of lithium, the promoter can physically cover the active sites in hydrocarbon formation, as indicated by the higher ratio of C<sub>2</sub> oxygenates to C<sub>2+</sub> hydrocarbons (Table 3, catalysts V, IV and III respectively).

TABLE 3

Selectivity ratio of hydrocarbons and oxygenated products on 3% Pd/*x*% Li/CeO<sub>2</sub>.

Parameter	Catalyst					
	Ia	Ib	II	III	IV	V
Hydrocarbon selectivity	9	63.4	56.1	74.2	79.1	63
Oxygenates selectivity	91	36.5	43.8	25.5	20.9	37
Oxygenates hydrocarbons	9	0.58	0.78	0.34	0.26	0.59
C <sub>2</sub> oxygenates/C <sub>2+</sub> hydrocarbons	—	—	0.22	0.78	0.68	3.2

TABLE 4

Concentration of formyl species on 3% Pd-*x*% Li/CeO<sub>2</sub>

Catalyst	Ib	II	III	IV	V
Formyl concentration (10 <sup>-6</sup> mol g <sub>cat</sub> <sup>-1</sup> )	2.20	11.13	5.02	0.94	2.76

*Chemical trapping*

In order to understand the influence of the promoter on the reaction intermediates, chemical trapping of surface formyl species was performed on a prerduced catalyst after treatment with carbon monoxide (30 min at 523 K). The concentration of formyl species versus different percentages of lithium on Pd/CeO<sub>2</sub> is shown in Table 4 and Fig. 2A.

Formyl species have been stated to be the main intermediate on palladium catalysts in many publications. A correlation between formyl species and methanol activity was found by Hindermann and co-workers [10,29]. TPD [30] and spectroscopic studies [31] after methanol or carbon monoxide-hydrogen Pd(111) have shown that methanol is decomposed into carbon monoxide probably through a formyl intermediate [32]. More recently, Diagne et al. [12] observed that, on Pd/CeO<sub>2</sub>, formyl species may also be the main intermediate in the decomposition of methanol.

As shown in Table 4, formyl species first increase with low lithium loadings (maximum at 0.15% lithium). It is noteworthy that the concentration of formyl species increases simultaneously with methanol production (Table 2, Fig. 2B) and with the amount of adsorbed carbon monoxide (Table 1, Fig. 2C). As proposed by Blyholder et al. [11] and Kiennemann et al. [29], the promoter stabilizes the formyl species by interacting with its oxygen. If this interaction becomes stronger it may reduce the carbon monoxide bond order and favour its dissociation and thus CH<sub>x</sub> species may be formed.



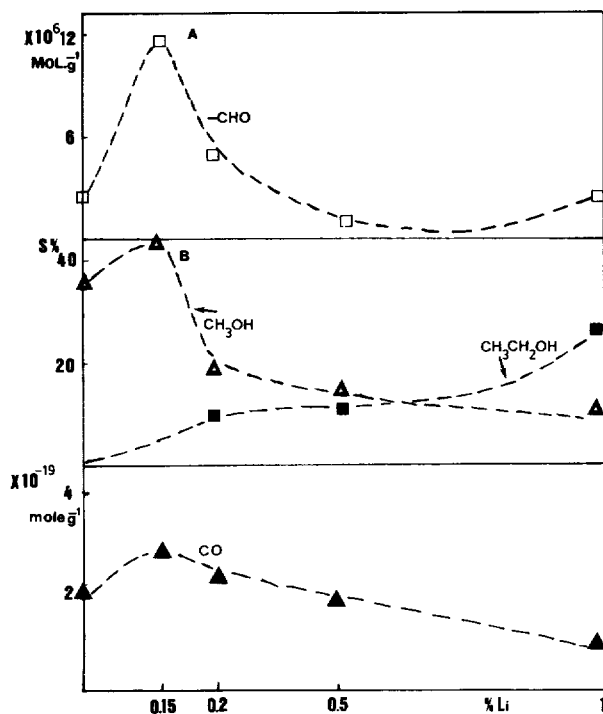


Fig. 2. Influence of lithium on (A) formyl concentration, (B) methanol selectivity and (C) carbon monoxide chemisorption.

At high percentages of lithium (e.g., 3% Pd-1% Li/CeO<sub>2</sub>), the concentration of formyl species increases again. An explanation can be that formyl species could participate in ethanol synthesis, as proposed by Breault [33], who indicated that on Rh-CeO<sub>2</sub>/SiO<sub>2</sub> catalysts formyl species are key intermediates between methane and ethanol, and the same proposition was made by van der Riet et al. [34] for cobalt catalysts.

In summary, Table 1 and Fig. 2 show that there is a link between methanol selectivity, formyl species and carbon monoxide chemisorption. There is no correlation between carbon monoxide chemisorption and ethanol synthesis.

### *Temperature-programmed desorption*

#### *After CO + 2H<sub>2</sub> reaction on 0.25% Li/CeO<sub>2</sub> (Fig. 3A)*

It is well known that methanol is formed by CO + 2H<sub>2</sub> reaction on CeO<sub>2</sub> alone [35], but with a conversion about one order of magnitude lower than on Pd/CeO<sub>2</sub> [12]. A TPD experiment was therefore performed on 0.25% Li after CO + 2H<sub>2</sub> reaction. CH<sub>3</sub>OH, CO<sub>2</sub>, CO and CH<sub>4</sub> were desorbed.

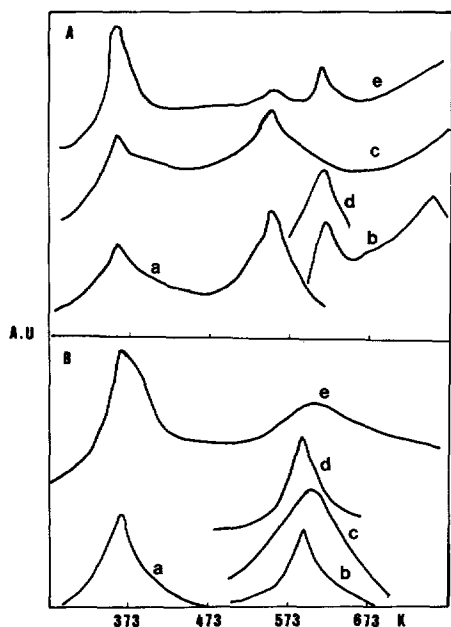
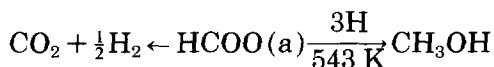


Fig. 3. TPD after carbon monoxide-hydrogen reaction: (A) on 0.25% Li/CeO<sub>2</sub>; (B) on 3% Pd-0.25% Li/CeO<sub>2</sub>. (a) CH<sub>3</sub>OH; (b) CH<sub>4</sub>; (c) CO<sub>2</sub>; (d) CO; (e) total response.

**Methanol desorption.** As observed on CeO<sub>2</sub> alone [12], two methanol desorption peaks appear. The first, at about 353 K instead of at 383 K on CeO<sub>2</sub> alone, can probably be attributed to the hydrogenation of a surface methoxy group. The second, at 543 K, could come from formate hydrogenation (formate can be formed by methanol oxidation on the surface). It corresponds to methanol desorption (540–550 K) on CeO<sub>2</sub> alone after formic acid adsorption [12].

**Carbon dioxide desorption.** The first carbon dioxide desorption peak at 353 K (low temperature) can be ascribed either to carbon dioxide formed during the CO + H<sub>2</sub> reaction and adsorbed on the surface or to the oxidation of carbon monoxide by CeO<sub>2</sub> similarly to that observed on ZnO [36]. A second peak, near 543 K, simultaneously with methanol desorption could come from formate decomposition as follows [(a) stands for adsorbed]



At 613 K, simultaneous desorption of carbon monoxide and methane is observed. It is noteworthy that Diagne et al. [12] found carbon monoxide and methane desorption peaks in that range (610–615 K) by TPD after formic acid adsorption on CeO<sub>2</sub> at the same temperature.

At 753 K, a methane desorption peak appears which can probably be ascribed to the hydrogenation of surface carbon produced by dissociation of carbon monoxide on  $\text{CeO}_2$  as proposed by Sudhakar and Vannice [37]. This phenomenon can be enhanced in the presence of lithium.

In general, the amount of desorption products is lower than that observed on  $\text{CeO}_2$  alone. This could be attributed to the decrease in the BET surface area due to the presence of lithium, as was suggested for lithium-doped silica by Kelly et al. [26].

*After  $\text{CO} + 2\text{H}_2$  reaction on 3% Pd-0.25% Li/ $\text{CeO}_2$  (Fig. 3B)*

The same desorption products as on 0.25% Li/ $\text{CeO}_2$  were observed, i.e.,  $\text{CH}_3\text{OH}$ ,  $\text{CO}_2$ , CO and  $\text{CH}_4$ .

*Methanol desorption.* Only one methanol desorption peak is observed at 363 K (with traces of ethanol), which can probably be ascribed to surface alkoxy hydrogenation. Unlike the results on 0.25% Li/ $\text{CeO}_2$  no methanol desorption occurs at higher temperatures. A similar result was obtained on Pd/ $\text{CeO}_2$  [12].

*Carbon monoxide and methane desorption.* On the lithium-doped catalyst, carbon monoxide desorption occurs at 590 K instead of at 470 K for the unpromoted catalyst. This significant shift in the carbon monoxide desorption temperature can probably be explained by the interaction of carbon monoxide adsorbed on palladium with lithium cation. Indeed, a similar increase in desorption temperature was observed by Berko et al. [38] in TPD after adsorption of carbon monoxide on potassium-predosed Pd(111).

*Carbon dioxide desorption.* An important peak of carbon dioxide desorption is observed at a slightly higher temperature than for carbon monoxide and methane desorption (603 K compared with 590 K). No carbon dioxide desorption was detected on Pd(111) [30] and on Pd/ $\text{SiO}_2$  or Pd/ $\text{CeO}_2$  after methanol adsorption [12] at this temperature. Therefore this carbon dioxide is, in our opinion, formed by the oxidation of carbon monoxide on the surface by a LiO species. This result is in agreement with those of Egawa et al. [39] on Pd(100) doped with sodium and sodium oxide; they concluded that the addition of one oxygen from the oxidic support to adsorbed carbon monoxide is promoted by the presence of sodium, thus leading to formate entities which decompose into carbon dioxide and hydrogen.

*Temperature-programmed desorption after ethanol adsorption*

*3% Pd-1% Li/ $\text{SiO}_2$  (Fig. 4A).* The influence of lithium on the decomposition of ethanol was studied first on a silica-supported catalyst. Ethanol, acetaldehyde, methane and carbon dioxide were desorbed after ethanol adsorption.

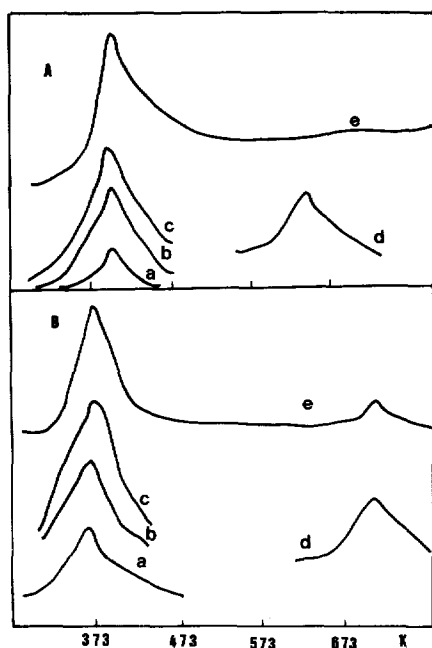


Fig. 4. TPD after ethanol adsorption: (A) on 3% Pd-1% Li/SiO<sub>2</sub>; (B) on 3% Pd-1% Li/CeO<sub>2</sub>. (a) CH<sub>3</sub>CHO; (b) CH<sub>3</sub>CH<sub>2</sub>OH; (c) CH<sub>4</sub>; (d) CO<sub>2</sub>; (e) total response.

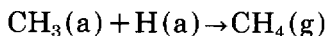
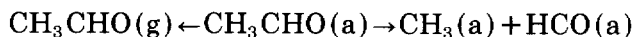
Ethanol, acetaldehyde and methane are evolved at the same temperature (about 393 K). Ethanol is probably formed by hydrogenation of ethoxy species on the palladium surface. On Pd/SiO<sub>2</sub>, ethanol evolved at 355 K and decomposed into methane and acetaldehyde (in small amounts) (383 K); no carbon monoxide is observed. Davis and Barteau [30] found that ethanol is decomposed into methane (350 K), hydrogen (350 K) and carbon monoxide (490 K) on Pd(111). No difference could be observed in the nature of the desorbed products after adsorption of methanol on Pd/SiO<sub>2</sub> [12] and Pd(111).

Acetaldehyde is thought to be an intermediate in C<sub>2</sub> alcohol synthesis [29] and decomposition [30]. It can therefore be produced by the dehydrogenation of the same ethoxy species. This dehydrogenation occurs through the cleavage of the carbon-hydrogen bond, which is consistent with the bond-breaking sequence on Ni(111) [40,41] and Ni(110) [42]. As acetaldehyde was not observed on Pd(111) after ethanol adsorption [30], it can be concluded that lithium probably decreases the rate of acetaldehyde dissociation and hence the latter can desorb before being further decomposed. Such a stabilization was observed on potassium-doped Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [40,43] and predicted on Li-Fe complexes for formyl species [11]. High-resolution electron energy loss spectroscopy (HREELS) studies of aldehyde adsorption on Ru(001) [44,45] and

Pt [46] have shown that an  $\eta^2(\text{C},\text{O})$  coordination is involved in the decomposition of aldehydes on metals.

Finally, methane can be formed by the hydrogenation of the methyl species resulting from acetaldehyde decomposition.

The following scheme can be proposed for ethanol decomposition:

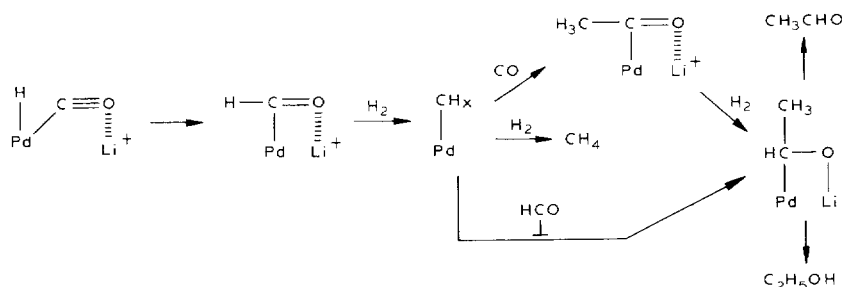


However, the formation of an acyl species as a decomposition intermediate cannot be excluded.

Carbon dioxide is released at 645 K from the 3% Pd-1% Li/SiO<sub>2</sub> catalyst, whereas carbon monoxide is desorbed from Pd(111) [30]. Carbon dioxide can either be formed by oxidation of carbon monoxide by LiO species or by the decomposition of a formate species, which can result from the oxidation of the formyl group. Indeed, Egawa et al. [39] observed that on sodium-doped Pd(100) formate entities are formed on adsorption of formaldehyde.

3% Pd-1% Li/CeO<sub>2</sub> (Fig. 4B). TPD after ethanol adsorption gave ethanol, acetaldehyde, methane and carbon dioxide. The product distribution is nearly the same as that on 3% Pd-1% Li/SiO<sub>2</sub>. However, two differences in the desorption temperatures exist: the simultaneous desorption of ethanol, acetaldehyde and methane occurs at a lower temperature (363 K); and carbon dioxide desorption takes place at a higher temperature (about 700 K).

In summary, the following mechanism is proposed for ethanol and methane formation on 3% Pd-*x*% Li/CeO<sub>2</sub> catalysts.



The interaction of carbon monoxide adsorbed on palladium with lithium can favour the formation of formyl species: the formyl species is stabilized by the presence of lithium (or an alkaline earth metal) as proposed by Blyholder et al. [11] and Hindermann et al. [10]; the formyl species can be hydrogenated into methanol or undergo a C-O bond cleavage to form  $\text{CH}_x$ ;  $\text{CH}_x$  species can

be hydrogenated into methane or react with an other adsorbed carbon monoxide molecule of a formyl species to produce ethanol, probably through an  $\eta^2(\text{C},\text{O})$  adsorbed acetaldehyde.

The mechanism of formation of  $\text{C}_2$  oxygenates on rhodium-containing catalysts has been discussed by different workers. Ichikawa and Fukushima [47] and Orita et al. [48] have shown by labelling experiments that on these catalysts there is only a minor contribution from methanol homologation for  $\text{C}_2$  oxygenates on silica-supported Rh and Rh-Ti catalysts. The  $\text{CH}_3$  group of  $\text{CH}_3\text{CH}_2\text{OH}$  is supplied by carbon monoxide dissociation and a subsequent insertion reaction of carbon monoxide provides a precursor of  $\text{C}_2$  oxygenates. Takeuchi and Katzer [49] studied the mechanism of methanol formation on a Rh/ $\text{TiO}_2$  catalyst by use of a mixture of  $^{13}\text{C}^{16}\text{O}$  and  $^{12}\text{C}^{18}\text{O}$ , and observed that methanol synthesis occurs by a non-dissociative mechanism. Sachtler and Ichikawa [50] ascribed the difference in selectivity and activity to two different mechanisms. On highly oxophilic promoter-containing catalysts the carbon monoxide dissociation and the insertion rate are enhanced, possibly through direct interaction of the oxygen atom of tilted adsorbed carbon monoxide. With basic oxides the blocking of dissociation sites was shown to be responsible for the inhibition of C-O dissociation. Changes in the temperature of this dissociation were observed by Ichikawa et al. [51] and Sachtler and Ichikawa [50] with the different promoters. These changes were linked to the appearance of bands at  $1760\text{ cm}^{-1}$  on Rh-Ti,  $1670\text{ cm}^{-1}$  on Rh-Zr and  $1735\text{ cm}^{-1}$  on Rh-V [50], which were attributed to a C and O bonded CO. Furthermore, in situ IR spectra at 31 bar and  $230\text{--}270^\circ\text{C}$  showed distinct bands at  $1672\text{--}1682\text{ cm}^{-1}$  (Rh-Mn),  $1620\text{ cm}^{-1}$  (Rh-Ti),  $1654\text{ cm}^{-1}$  (Rh-Fe) and  $1650\text{ cm}^{-1}$  (Rh-Zr) [50,52,53], which were ascribed to an acyl species.

This mechanism is very similar to ours. The only difference is that the C-O bond is proposed to be cleaved only after hydrogenation, as palladium is considered by many workers to adsorb carbon monoxide non-dissociatively. However, the dissociation of carbon monoxide cannot be excluded, as the interaction of the oxygen end of CO with the support weakens the C-O bond and therefore must favour its dissociation.

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