



## Palladium-based catalysts for the synthesis of alcohols

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### Abstract

The present work intends to illustrate the effects of precursor and support composition on the structure and performance of Pd-based catalysts for the synthesis of methanol and higher oxygenated compounds. The power of the XRD technique and the reaction itself, as characterisation tools, was evidenced.

The hydrogenation of carbon monoxide has been studied over palladium supported on ZnO, Zr(OH)<sub>4</sub> and ZrO<sub>2</sub> using PdCl<sub>2</sub> and Pd(NO<sub>3</sub>)<sub>2</sub> as salt precursors. Catalysts were characterised by XRD and Raman spectroscopy. The results show that activity and selectivity are strongly dependent on the salt precursor and on the acid–basic properties of the support. As seen from the CH<sub>3</sub>OH/DME ratio, the order of acidity of the supports is: Zr(OH)<sub>4</sub> > ZrO<sub>2</sub> > ZnO independently of the salt precursor used. The Pd(NO<sub>3</sub>)<sub>2</sub>/ZnO catalyst shown the highest methanol selectivity which was related to the presence of large particles of a PdZn alloy.

A double bifunctionality on the catalysts for the production of higher oxygenated seems evident. On the one hand, an acid–base bifunctionality of the support seems to be needed for the formation, stabilisation, chain growth and further reactivity of intermediates such as formate, as well as for the dissociative adsorption of CO, and on the other hand, a metal–support bifunctionality, where the palladium metal particles would play the role of hydrogenating the intermediates and possibly adsorb non-dissociatively the CO.

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### 1. Introduction

Many papers have been written since Poutsma et al. [1] reported for the first time, that hydrogenation of

carbon monoxide over supported palladium catalysts produced methanol in high selectivity. They suggested that the ability of palladium to catalyse methanol formation under elevated pressures results from its excellent hydrogenation ability coupled with its inherent tendency to adsorb CO non-dissociatively even at reaction temperatures.

The reason for the continuous interest on the study of palladium-based catalysts on the CO hydrogenation

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reaction comes from the fact that they provide an alternative to the presently used copper-based catalysts as they possessed tolerance towards sulphur poisoning [2,3].

From all the work published after Poutsma et al. [1], major advances have been made in our understanding of palladium-based systems.

It is clear now that the catalytic properties of palladium for CO hydrogenation are quite sensitive to the nature of the support, the presence of promoters, the palladium particle size and the metal precursor. However, the way in which each of these parameters affect the behaviour of palladium-based catalysts remains a subject of controversy.

From the pioneer work of Fajula et al. [4], it was clear that the nature of the support was crucial to obtain methanol. They studied palladium supported on Y zeolite and on three different commercial SiO<sub>2</sub>. Their first observation was that under their experimental conditions (270–290 °C and 15–16 atm) the selectivity, the activity and the stability of their catalysts were strongly dependent on the type of support used. Depending on the source and grade of the silica used a 20-fold variation and a nearly 100% variation in selectivity towards methanol was observed.

On how the support was affecting the performance of palladium catalysts was then the subject of major debate. The explanation of Fajula et al. [4] in their work was that methanol synthesis was favoured on small metal crystallites where CO was weakly adsorbed while methane formation was enhanced when the density of acidic sites at the surface of the support was high.

Hick and Bell [5] reported on the effect of support on palladium morphology as expressed by the distribution of Pd(1 0 0) and Pd(1 1 1) planes determined from “in situ” infrared spectra of adsorbed CO. They observed that the crystallite morphology of a Pd/SiO<sub>2</sub> catalyst was the same independently of palladium loading: 90% of the surface was comprised of Pd(1 0 0) planes and 10% of the surface was comprised of Pd(1 1 1) planes. By contrast, the crystallite morphology of a Pd/La<sub>2</sub>O<sub>3</sub> catalyst changed with palladium loading. Primarily Pd(1 0 0) planes were exposed at low-weight loading while Pd(1 1 1) planes were exposed at high-weight loading. They observed that the palladium morphology influences the specific activity of Pd/La<sub>2</sub>O<sub>3</sub> for methanol synthesis: Pd(1 0 0) was

nearly three-fold more active than Pd(1 1 1). However, for a fixed morphology, the specific methanol synthesis activity of Pd/La<sub>2</sub>O<sub>3</sub> was a factor of 7.5 greater than that of Pd/SiO<sub>2</sub>. A metal-support interaction was claimed to be responsible for these results.

Jackson et al. [6] reported on the effect of using molybdenum and tungsten trioxides as supports for the medium pressure CO hydrogenation over group VIII metals. All metals tested, except iron, showed activity enhanced by up to two-fold orders of magnitude when either molybdenum or tungsten trioxide replaced silica as support. They suggested that under reaction conditions, a fast spillover/reverse spillover of hydrogen occurred between the metal and the support and they stated that this process allowed an effective hydrogen concentration increase to the reactive intermediates and hence, causes an enhancement of the rates. No comments were made regarding the product distribution but it can be seen from their results that on Pd/SiO<sub>2</sub> catalysts, methanol was the main product while when WO<sub>3</sub> was used as support, selectivity shifted towards methane. Dimethylether formation was obtained on Pd/WO<sub>3</sub> but the authors do not mention any acidity effect.

CO hydrogenation on supported palladium catalysts was investigated by Ali and Goodwin [7] using Steady-State Isotopic Transient Kinetic Analysis (SSITKA) in order to explore the differences in the catalytic behaviour resulting from the use of different supports with different acidities (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>·Al<sub>2</sub>O<sub>3</sub>). The nature of the support significantly altered the activity and selectivity of palladium. The order of activities at steady state for a given precursor was Al<sub>2</sub>O<sub>3</sub> > SiO<sub>2</sub>·Al<sub>2</sub>O<sub>3</sub> > SiO<sub>2</sub>. It was found that Pd/SiO<sub>2</sub> produced essentially only methanol. The use of acidic supports (Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>·Al<sub>2</sub>O<sub>3</sub>) resulted in the formation of dimethylether which was limited by the amount of methanol formed. Palladium on acidic supports produced significant amounts of methane. The SSITKA results showed that the nature of the support altered only slightly the intrinsic activity of the sites producing methane and methanol. However, the number of surface intermediates leading to methane and methanol were significantly affected by the support used. They concluded that the impact of the support on the reaction rate was determined by its effect on the concentration of active sites/intermediates on palladium.

From the above discussion, it seems to be a consensus on the fact that acidity on the support favours the rate of methane formation and enhances overall activity. The fact that a Pd/SiO<sub>2</sub> catalyst (which is rather a neutral support) produced almost exclusively methanol was not related to any property of the support. A clearer picture on this respect arises when the promoters/impurities effect is reviewed.

Gotti and Prins [8] prepared Pd and Rh catalysts using an ultra pure SiO<sub>2</sub> doped with Al, Fe, Na, K, or Ca in order to investigate their activity and selectivity on the CO hydrogenation reaction. They observed that additives had a strong influence on the catalytic properties. The doping with alkali and alkaline earth oxides led to a strong suppression of the CO dissociation. Particularly, basic additives, such as calcium had an strong promoting effect on the methanol formation. In another work, the same authors [9] stated that molecular adsorption of CO or CO<sub>2</sub> and the availability of activated hydrogen are not sufficient to form methanol: basic metal oxides are needed to give palladium a high methanol activity. In addition, the basic oxide additives must be close to or in contact with the palladium particle to be effective in methanol synthesis. Furthermore, the clear correlation between calcium amount, noble metal surface and C1-oxo activity may confirm that the formation of methanol occurs through formate intermediates formed by the reaction of CO with the basic support or at the interface between the promoter oxide and the noble metal particle. From their results, they concluded that the rate enhancement for methanol formation of the metal oxides followed a volcano curve when plotted as a function of the metal ion electro negativity, with a maximum for metal oxides with a moderate basic nature.

In an earlier work, Nonneman et al. [10,11] shown that, not only by adding alkaline promoters to the metallic catalysts it was possible to enhance methanol formation but that impurities on the support could play an important role as they can be leached out during the impregnation step and promote the metal sufficiently to produce methanol and higher oxygenates.

The prevalent opinion is that the promoter should be located on or close to the noble metal surface, probably as oxide patches [12] and that the presence of basic promoters like calcium, close or on the active metal particle has a strong promoting effect on the methanol production.

A more recent work of Gusovius et al. [13], where the study of a series of calcium promoted Pd/SiO<sub>2</sub> catalysts with different calcium loading was reported suggested that (i) calcium locates itself preferentially on the palladium particles (rather than on the support) and (ii) that calcium species located on (and perhaps also near) the palladium particles give rise to the catalytic activity for C1-oxo. Moreover, the requirement for the promoter to be located on the palladium particle means that an effective promoter must not only have favourable chemical properties for the reaction but must also have a high affinity for the metal particle and its oxidic precursor.

Particle size have also an influence on the performance of palladium catalysts [4,5,14–17]. When a reaction is structure sensitive, formation of smaller particles on supported catalysts is of considerable importance as the catalytic surface area is enlarged and, as a consequence, the catalytic activity is enhanced. Kim et al. [14,15] reported the study of the CO hydrogenation reaction over palladium catalysts prepared by a water-in-oil micro emulsion method developed by them, with the aim of producing well-dispersed catalysts. They reported a size distribution of palladium particles remarkably narrow with an average particle size much smaller than that found when conventional wet impregnation method was used. A drawback of this method of preparation was that some of the palladium particles were wholly or partially embedded in the support. However, the catalysts prepared by the micro emulsion method were found to exhibit a much higher activity (three times as high) for the CO hydrogenation reaction than the catalysts prepared by impregnation. Product selectivity was considered to be independent of the palladium particle size. The same conclusion was reported by Kirillov and Ryndin [16]. Gotti and Prins [8] on the other hand reported a greater promoter-metal contact area for catalysts with a small noble metal particles which results in a more efficient promotion of the methanol formation.

An earlier work of Rieck and Bell [17] has shown that dispersion had an effect on the interaction of H<sub>2</sub> and CO with Pd/SiO<sub>2</sub>. They reported that the distribution of H<sub>2</sub> ad-states changes with dispersion due possibly to a change on the morphology of the palladium crystallites or in the co-ordination of adsorbed H atoms. For the CO adsorption, these authors state that the ratio of linearly held CO to bridge-bonded

CO decreases with the dispersion, as does the ratio of Pd(100) to Pd(111) planes on the surface of the palladium crystallites. It was concluded that CO dissociation occurs preferentially from bridged sites and proceeds more readily with decreasing dispersion. Consistent with this, the turnover frequency for methanation increases with decreasing dispersion.

Dispersion may be influenced by the salt precursor used although there is not consensus on its real effect. Gotti and Prins [8] reported a dramatic influence of the salt precursor for the Pd/SiO<sub>2</sub> catalysts. Catalysts prepared from PdCl<sub>2</sub> and Pd(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> had a higher hydrocarbon activity than when prepared from Pd(NO<sub>3</sub>)<sub>2</sub>. This observation correlates with strong differences in metal dispersion. Apparently, the CO dissociation is only favoured on small palladium particles and the metal salt anion has an indirect effect through its influence on the final metal dispersion. In contrast, Ali and Goodwin [7] stated that the palladium precursor had no apparent impact on palladium dispersion. However, these author reported that the total rate of CO conversion was somewhat higher for the catalysts prepared using PdCl<sub>2</sub> rather than Pd(NO<sub>3</sub>)<sub>2</sub> precursor at steady state.

From the latest studies, one can safely said that the major parameters which affect the performance of Pd catalysts are

1. the acid–base properties of the support;
2. the addition of promoters/additives;
3. the nature of the salt precursor.

The present work intend to give further evidence of the effects of the acid–base properties of the support and the nature of the salt precursor by means of XRD, Raman spectroscopy and the CO hydrogenation reaction itself.

## 2. Experimental

### 2.1. Catalysts preparation

The catalysts were prepared by incipient wetness impregnation using as supports a commercial Zr(OH)<sub>4</sub> (MEL Chemicals, 310 m<sup>2</sup>/g), ZrO<sub>2</sub> which was obtained by calcination of the former at 500 °C (ramp 3 °C/min) for 15 h (43 m<sup>2</sup>/g) and ZnO synthesised following the method described by Cubeiro and Fierro [18].

For the synthesis of ZnO, a solution of oxalic acid [H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, Riedel de Haen, 4, 5 ml de H<sub>2</sub>O/g H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O] was added drop wise under continuous stirring to a zinc nitrate solution [Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Riedel de Haen, 0, 18 ml H<sub>2</sub>O/g Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O] at room temperature. The resulting zinc oxalate (ZnC<sub>2</sub>O<sub>4</sub>), was left on digestion for 12 h, filtered dried at 110 °C for 24 h and calcined at 400 °C (ramp 2 °C/min) for 3 h to finally obtain a ZnO with a surface area of 24 m<sup>2</sup>/g. All supports were impregnated with both, an aqueous solution of Pd(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O [Strem Chemical-named Pd(N)/support] and HCl acidified aqueous solution of PdCl<sub>2</sub> [Aldrich, 0, 3 g de PdCl<sub>2</sub>/ml HCl-named Pd(C)/support] dried at 110 °C overnight and calcined in air at 400 °C (ramp 2 °C/min) for 3 h to give a nominal content of 3% Pd (w/w).

### 2.2. Catalysts characterisation

Surface area of the supports and catalysts were obtained from nitrogen adsorption and desorption at 77 K in a Micromeritics Flow Sorb II 2300, using a N<sub>2</sub>–Ar (30% N<sub>2</sub>) gas mixture. For the analysis, 20 mg of the samples were heated at 200 °C for 2 h under flowing nitrogen. Palladium loadings were determined by inductively-coupled plasma-atomic emission spectrometry (ICP-AES).

“In situ” programmed temperature XRD data for structural analysis and particle size determination were collected with a Siemens D5000 diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) by placing the solids on a gold sample holder at  $2\theta = 20\text{--}60^\circ$  with a  $0.02^\circ$  step size. Background correction, K $\alpha_2$  stripping and peak identification was accomplished with the Diffract AT program from Siemens. The mean particle size was derived from XRD line broadening, using the simple Scherrer equation.

Raman spectra were recorded using a Dilor XY monochromator with subtractive dispersion. The samples were excited using a 632.8 nm radiation of a He–Ne laser. The samples were analysed under atmospheric pressure after being calcined in air at 400 °C.

### 2.3. Activity testing

Catalysts were tested for hydrogenation of CO using a 40 cm, 1/2 in a 316 stainless steel reactor. In order to

avoid contamination of the catalysts with Fe carbonyls coming from the gas cylinder, an activated carbon trap was placed upstream of the catalyst to adsorb such metal carbonyls. A mixture of H<sub>2</sub>:CO:N<sub>2</sub> (63:32:5) was fed from a mass flow controller (Brooks Instruments 5850E). Nitrogen was used as internal standard. The catalyst (600 mg) was placed in the centre of the reactor between two beds of glass beads separated from the catalyst bed by glass wool. Downstream of the reactor the line was kept at 120 °C to avoid product condensation. The catalysts were reduced in a flow of H<sub>2</sub> (50 ml/min) at 400 °C (ramp 2 °C/min) for 3 h under atmospheric pressure. Pressure was increased to working pressure (50 bar) using the H<sub>2</sub>:CO:N<sub>2</sub> mixture by means of a back pressure regulator. Reaction temperature (280–350 °C) was reached as the pressure was increased. In all cases, the reaction started at 280 °C and temperature was increased every 24 h to reach 320 and 350 °C. The data reported in the present paper are the corresponding to a reaction temperature of 320 °C. Space velocity was 5.000 ml/(g<sub>cat</sub> h). Experiments were carried out for 72 h on stream. The reactor effluents were analysed every hour using an on line Varian 3300 gas chromatograph equipped with a Carbosieve SII column (SS, 12 ft. × 1/8 in.) and a TCD detector for analysis of CO, N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> and a Chrompack CP 9100 gas chromatograph equipped with a Quadrex Corp methyl silicon capillary column (fused SiO<sub>2</sub>, 50 m × 0.32 mm) and a FID detector for analysis of the hydrocarbons and oxygenated compounds. CO conversion was determined using nitrogen as an internal standard. Chromatograms were correlated through methane and selectivities were obtained based on converted carbon.

### 3. Results and discussion

Table 1 shows the chemical analyses and surface area of all the prepared catalysts. In all cases, the real content was very similar to the nominal one. The catalysts maintain similar surface areas as compared with that of the support, with the exception of the catalysts supported on Zr(OH)<sub>4</sub> where values are half of the observed for the support, attributed to the fact that these catalysts were calcined at 400 °C. Under this condition, the Zr(OH)<sub>4</sub> partially crystallises leading to a reduction of the surface area.

Table 1  
Chemical analyses and surface area

Catalyst	Pd (%)	Zr (%)	Zn (%)	Surface area (m <sup>2</sup> /g)
Pd(N)/ZnO <sup>a</sup>	2.78	–	79.65	21
Pd(C)/ZnO <sup>a</sup>	2.65	–	75.00	21
Pd(N)/Zr(OH) <sub>4</sub> <sup>b</sup>	3.73	65.53	–	146
Pd(C)/Zr(OH) <sub>4</sub> <sup>b</sup>	3.85	65.40	–	146
Pd(N)/ZrO <sub>2</sub> <sup>b</sup>	3.53	69.50	–	37
Pd(C)/ZrO <sub>2</sub> <sup>b</sup>	3.32	69.00	–	35

<sup>a</sup> Dried.

<sup>b</sup> Calcined.

#### 3.1. XRD results

Fig. 1 shows the evolution of the XRD patterns of Pd(N)/ZnO catalysts under reduction conditions. The characteristic signals of ZnO in a hexagonal structure (JCPDS 790205) are observed at room temperature which confirm that the synthesis method lead to a well crystallised ZnO. The signal at  $2\theta = 38.44^\circ$  is assigned to gold (JCPDS 040784) on the sample holder. When the sample is reduced, two additional bands at  $2\theta = 41.62$  and  $44.10^\circ$  are seen. These two signals are characteristic of a PdZn alloy (JCPDS 6-620). These results are in good agreement with those reported by Iwasa et al. [19] and by Cubeiro and Fierro [18]. With increasing temperature, better defined signals can be observed with the mean particle size increasing from 8 nm (at 250 °C) to 23 nm (at 450 °C). The presence of a signal at  $40.0^\circ$  assigned to palladium metal (JCPDS 5-681) can also be assessed from the diffractogram at 400 °C but not that of the metallic zinc. It cannot be ruled out, however, that some zinc metal could be present in small particles.

Fig. 2 shows the XRD pattern of the catalyst after reaction. No important changes are observed as compared with the reduced catalyst. The presence of the signals at  $41.62$  and  $44.10^\circ$ , evidence the presence of the PdZn alloy in the reacting catalyst.

Fig. 3 shows the evolution of the XRD patterns for the Pd(C)/ZnO catalyst under reduction condition. As in the Pd(N)/ZnO catalyst all the signals attributed to ZnO are present on the diffraction patterns although their intensity is lower. This could be due to the fact that, since an acid solution was used for the preparation of this catalyst, it is possible that some of the zinc oxide was partially dissolved, resulting in the

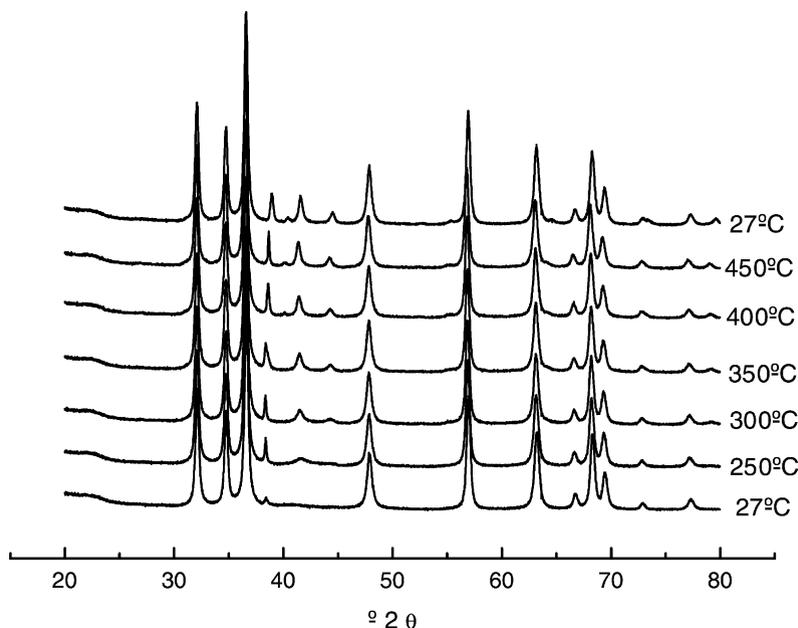


Fig. 1. Evolution of the XRD patterns of Pd(N)/ZnO catalysts.

formation of a new oxide phase or of zinc oxychloride after the thermal treatment with lower crystallinity. In contrast with the results observed for the Pd(N)/ZnO catalysts, the 41.62 and 44.10° signals attributed to the PdZn alloy can be only seen when the temperature reach 400 °C as compared with the apparition of the same signals at 250 °C for the Pd(N)/ZnO.

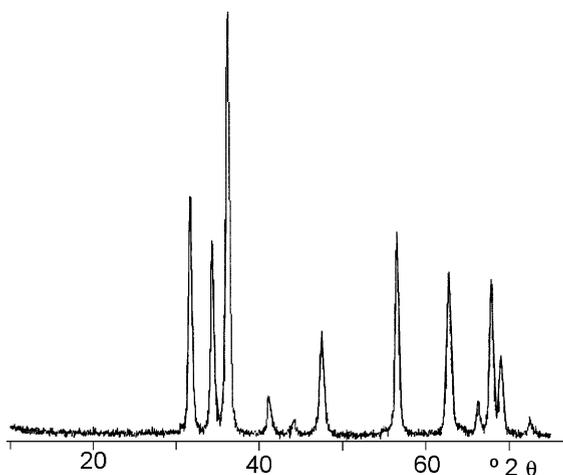


Fig. 2. XRD pattern of the Pd(N)/ZnO catalyst after reaction.

Fig. 4 shows the XRD pattern of Pd(N)/ZnO and Pd(C)/ZnO catalysts reduced at 400 °C (reduction temperature before reaction). The mean particle sizes as derived from the XRD line broadening are 21 nm and 9 nm, respectively. It is clear that smaller metal particles are obtained when PdCl<sub>2</sub> is used as palladium precursor, compared to catalysts prepared using Pd(NO<sub>3</sub>)<sub>2</sub>. Fig. 5 shows the Pd(C)/ZnO catalysts after reaction. In this case, the reacted catalyst did not show the presence of the signals assigned to the PdZn alloy. This fact seems to be an indication that the alloy is present in small particles. From the above discussion, it is possible to conclude that the PdZn alloy is formed regardless the precursor salt but the particle size is greatly affected by it.

The evolution of the XRD patterns of Pd(N)/Zr(OH)<sub>4</sub> catalyst with calcination temperature is shown in Fig. 6. At room temperature the signals attributed to ZrO<sub>2</sub> ( $2\theta = 30.3, 34.6$  and  $50.3^\circ$ ) in its tetragonal structure (JCPDS 79177) are present. It has to be pointed out that this catalyst was calcined at 400 °C before the analysis. When temperature is increased up to 700 °C, the original signals remain, becoming a little bit better defined.

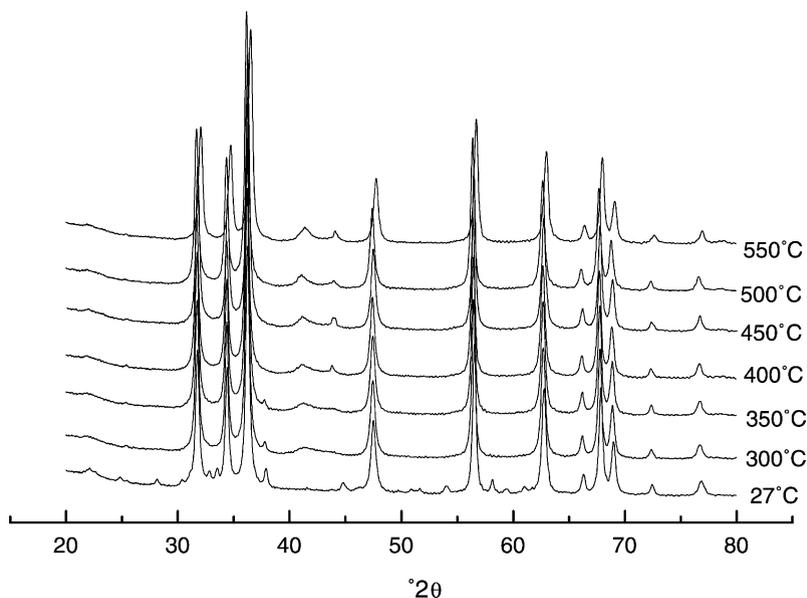


Fig. 3. Evolution of the XRD patterns of Pd(C)/ZnO catalyst.

During the cooling down process (last diffractogram at 27 °C), a new small signal appears at  $2\theta = 28.2^\circ$  assigned to  $\text{ZrO}_2$  in its monoclinic structure (JCPDS 371484). Additionally, when the temperature is increased up to 500 °C and upwards, three new signals appeared attributed to the tetragonal phase of PdO (JCPDS 431024): a shoulder at  $2\theta = 33.5^\circ$ , and other signals at  $2\theta = 41.9$  and  $54.7^\circ$ . After reaction, in ad-

dition to the signals assigned to the tetragonal phase of  $\text{ZrO}_2$ , signals at  $2\theta = 28.0^\circ$  attributed to the monoclinic phase and at  $2\theta = 40.0^\circ$  attributed to metallic palladium (JCPDS 5-681) were observed.

For the Pd(C)/Zr(OH)<sub>4</sub> catalyst, a poor crystallinity of the tetragonal phase of  $\text{ZrO}_2$  (signals at  $2\theta = 30.3$ ,  $34.6$  and  $50.3^\circ$ ) is observed (Fig. 7). In a previous work [20], we reported using TGA/TDA analyses that

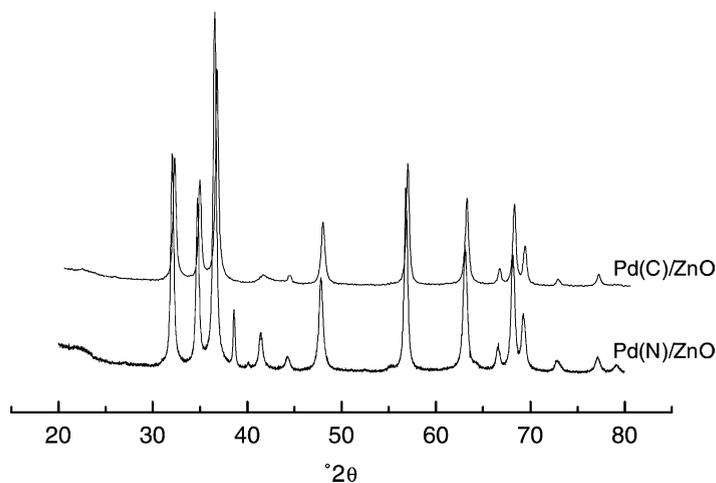


Fig. 4. XRD pattern of the Pd(N)/ZnO and Pd(C)/ZnO catalysts reduced at 400 °C.

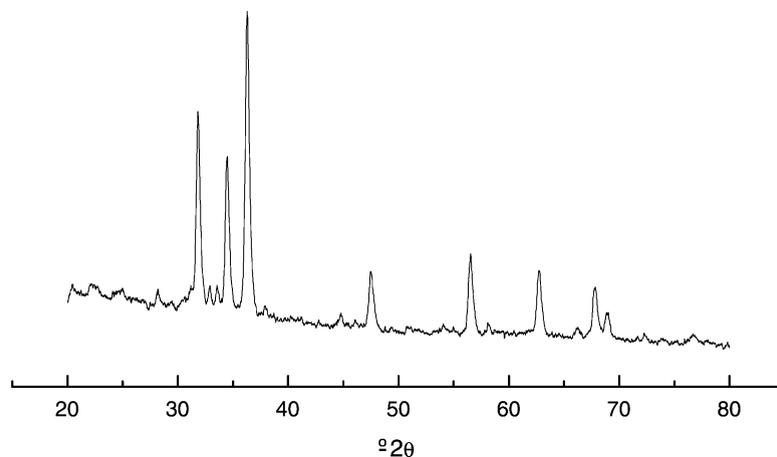


Fig. 5. XRD pattern of the Pd(C)/ZnO catalyst after reaction.

when using  $\text{Pd}(\text{NO}_3)_2$  as precursor salt crystallisation starts at  $425^\circ\text{C}$  while when using  $\text{PdCl}_2$ , crystallisation starts at  $484^\circ\text{C}$ . These results lead us to claim that crystallisation is retarded by the presence of chloride. As a consequence, the lack of crystallinity for  $\text{ZrO}_2$  is attributed to the need of a higher calcination temperature for this sample.

Another important feature in Fig. 7 is the absence of signals at  $2\theta = 41.9$  and  $54.7^\circ$  attributed to PdO. These results lead us to conclude that again, when using nitrate as precursor, the palladium particle size of the final catalyst is larger than those observed when using chloride as precursor. Again the monoclinic struc-

ture signal at  $2\theta = 28.8^\circ$  appears after cooling down. After reaction, the presence of a signal at  $2\theta = 40^\circ$  assigned to palladium metal in the catalysts prepared using  $\text{Pd}(\text{NO}_3)_2$  as precursor and its absence in the catalyst prepared using  $\text{PdCl}_2$  provided further evidence that the precursor salt has an effect on the palladium particle size of the final catalyst.

Fig. 8 shows the XRD patterns of the fresh Pd(N)/ $\text{ZrO}_2$  and Pd(C)/ $\text{ZrO}_2$  catalysts. For both Pd/ $\text{ZrO}_2$  catalysts, no much information can be drawn from the XRD results as the patterns are very rich in signals. The overlapping of the different diffraction peaks does not allow to evidence the presence of Pd neither PdO phases by XRD. Nevertheless, it can be said that for the Pd/ $\text{ZrO}_2$  catalysts the characteristic signals assigned to the monoclinic phase of  $\text{ZrO}_2$  at  $2\theta = 28.2$  and  $31.0^\circ$  are present along with a tetragonal phase signal at  $2\theta = 30.5, 34.6$  and  $50.3^\circ$ .

In order to overcome this problem and assess a possible difference in particle size or palladium crystallinity on Pd/ $\text{ZrO}_2$  catalysts, Raman spectrometry measurements were conducted as it has been reported in the literature that PdO shows a sharp band at around  $648\text{--}652\text{ cm}^{-1}$  [21–23].

Fig. 9 shows the Raman spectra for  $\text{ZrO}_2$ , Pd(C)/ $\text{ZrO}_2$  and Pd(N)/ $\text{ZrO}_2$  samples in the  $250\text{--}750\text{ cm}^{-1}$  range. The spectrum of pure zirconia exhibits the bands characteristics of  $\text{ZrO}_2$  in the monoclinic phase [22]. When  $\text{PdCl}_2$  salt is used, no changes in the spectrum are observed. This observation is an

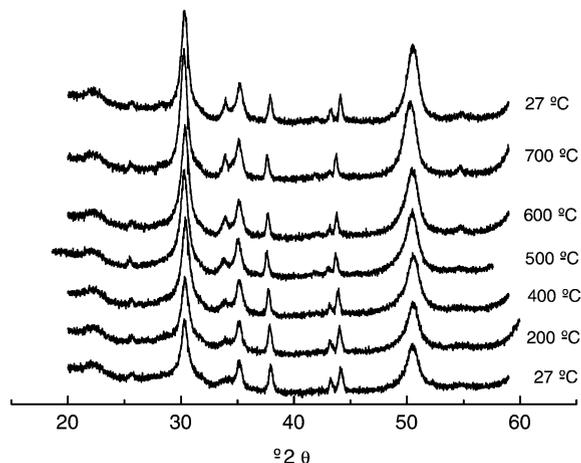


Fig. 6. Evolution of the XRD patterns Pd(N)/ $\text{Zr}(\text{OH})_4$  catalyst.

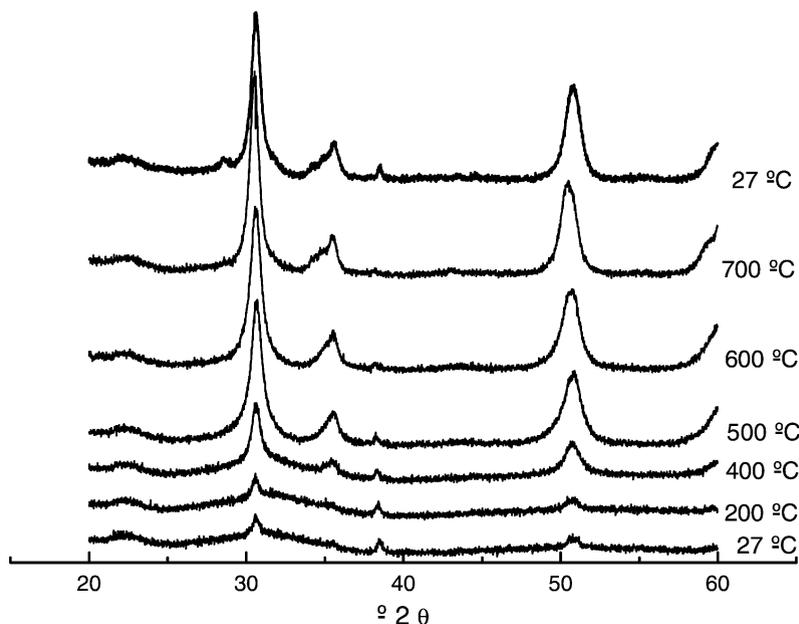


Fig. 7. Evolution of the XRD patterns Pd(C)/Zr(OH)<sub>4</sub> catalysts.

indication of a well dispersed palladium phase [21]. When Pd(NO<sub>3</sub>)<sub>2</sub> salt is used, a clear increase in the intensity of the band at 648 cm<sup>-1</sup> is observed. In this case, a contribution of the PdO phase seems to be an evidence of the presence of a better crystallised phase when the nitrate precursor is used. Again, the effect of the precursor salt on the crystallisation of palladium is assessed.

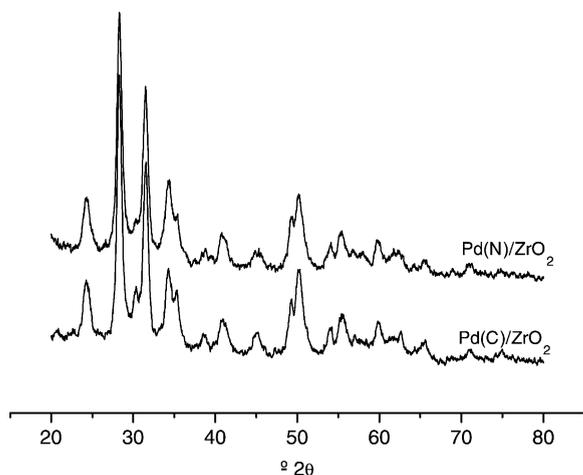


Fig. 8. XRD patterns of the Pd(N)/ZrO<sub>2</sub> and Pd(C)/ZrO<sub>2</sub> catalysts.

### 3.2. CO hydrogenation reaction results

Under the reaction conditions used ( $T_{\text{reaction}} = 320\text{ }^{\circ}\text{C}$ ,  $\text{SV} = 5000\text{ ml}/(\text{g}_{\text{cat}}\text{ h})$ ,  $P_{\text{reaction}} = 5\text{ MPa}$ ,  $\text{H}_2/\text{CO} = 2$ ) conversions were lower than 10%.

Fig. 10 shows the catalytic activity (mol CO/(kg Pd h)) for all the catalysts studied. In general, higher activities were obtained, when using PdCl<sub>2</sub>. Additionally, Pd/ZrO<sub>2</sub> catalysts were more active than Pd/Zr(OH)<sub>4</sub> and Pd/ZnO catalysts.

The fact that catalysts prepared with palladium chloride are more active can be related to particle size. As seen by the Raman and XRD results, the particle size of the palladium when using palladium chloride was smaller than that obtained when palladium nitrate was the precursor salt, so it is possible to conclude that differences in activities with precursor salt can be related to dispersion.

In addition of the salt precursor effect, the support seems to play an important role. The difference in activity showed when support was changed could be related either to its acid–base properties [9], its ability to chemisorbs CO dissociatively [8,24], to the presence of cationic palladium species formed through a metal–support interaction

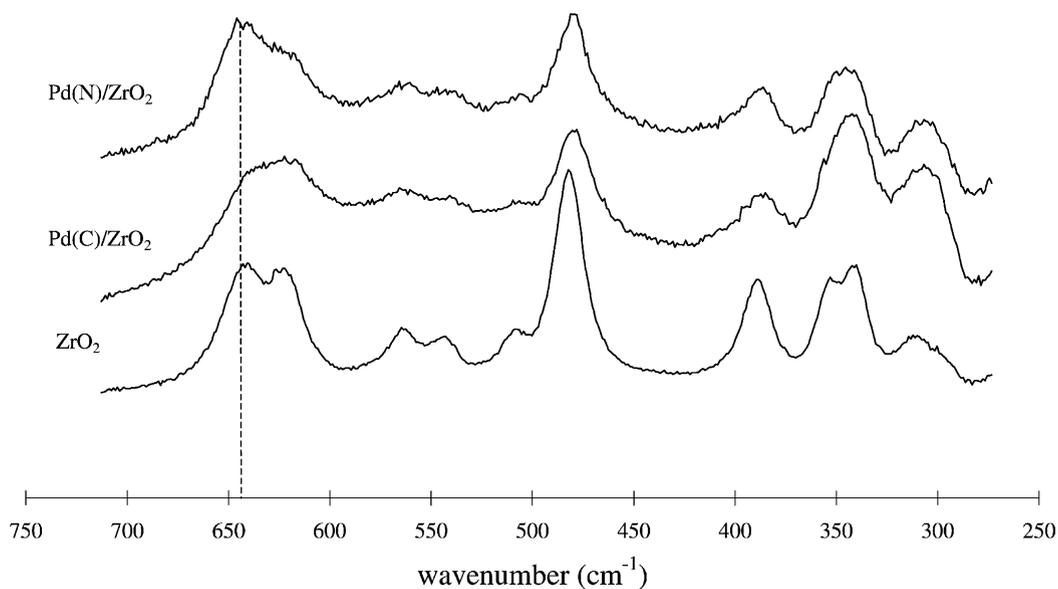


Fig. 9. Raman spectra for  $\text{ZrO}_2$ ,  $\text{Pd(C)/ZrO}_2$  and  $\text{Pd(N)/ZrO}_2$  samples.

as reported by Shen et al. [25] or again to metal dispersion.

The more active catalysts were those supported on zirconia. Two possible explanations could be given: (i) the reported ability of  $\text{ZrO}_2$  to chemisorb CO dissociatively [24] or, as reported by Gotti and Prins [9] and (ii) to its amphoteric character. On the other hand, it has been recently stated [26] that the CO adsorption capacity of  $\text{ZrO}_2$  depends on the crystallographic phase. The adsorption capacity of monoclinic  $\text{ZrO}_2$  was reported to be significantly higher than that of tetragonal  $\text{ZrO}_2$ . As seen on our XRD results, catalysts prepared on  $\text{Zr(OH)}_4$  had the  $\text{ZrO}_2$

in its tetragonal phase after calcination, while in the catalysts supported on  $\text{ZrO}_2$ , the former is present in its monoclinic phase. This can explain the differences in activity among  $\text{Pd/Zr(OH)}_4$  and  $\text{Pd/ZrO}_2$  catalysts. The lower activity observed for the  $\text{Pd/ZnO}$  catalysts could be related to the basic character of the support. Gotti and Prins [8] reported that basic sites led to a strong suppression of CO dissociation which, as stated above, does not contribute with gross activity. The particle size effect cannot be ruled out, especially because the presence of surface hydroxyls groups in the  $\text{Pd/Zr(OH)}_4$  catalysts could influence palladium deposition, controlling particle size. Evidence of this was reported elsewhere [20].

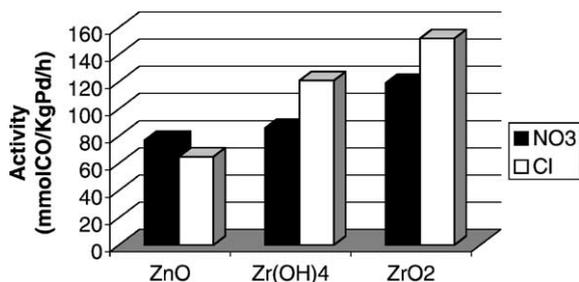


Fig. 10. Catalytic activity (mol CO/(kg Pd h)) of the catalysts as a function of support and salt precursor.

Figs. 11 and 12 show the product selectivity for the catalysts studied. The catalysts prepared using ZnO as support shows interesting results: while the  $\text{Pd(N)/ZnO}$  catalyst was very selective towards methanol formation (98% selectivity),  $\text{Pd(C)/ZnO}$  catalyst produced mainly methane (70% selectivity). The high methanol selectivity of the  $\text{Pd(N)/ZnO}$  could safely be attributed to the presence of large particles of the PdZn alloy as the XRD results evidenced the presence of larger particles of a PdZn alloy when  $\text{Pd(NO}_3)_2$  was used as precursor salt. Similarly, the high hydrocarbon formation obtained when using

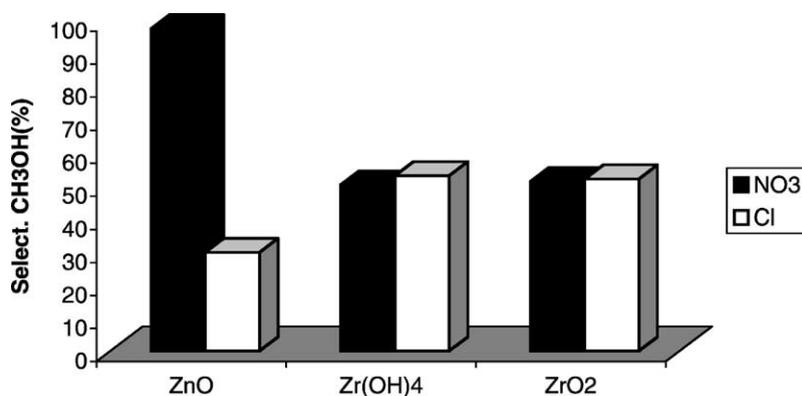


Fig. 11. Methanol selectivity as a function of support and salt precursor.

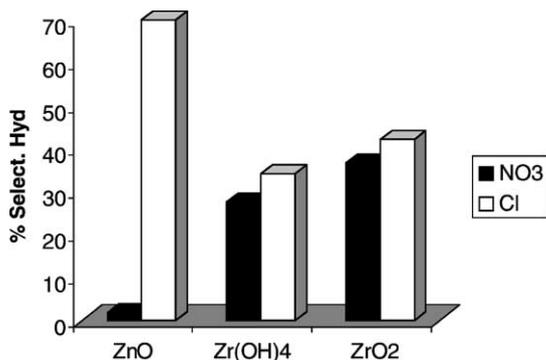


Fig. 12. Hydrocarbon selectivity as a function of support and salt precursor.

PdCl<sub>2</sub> could probably be explained relating it with the presence of small particles [8]. In order to obtain further evidence on the need of bigger PdZn alloy particles as a condition to have high methanol selectivity, the Pd(C)/ZnO catalyst was reduced at 600 °C using a higher heating rate with the aim of promote sintering (Table 2). The results obtained show a complete change of the product distribution and do not leave any doubt. A selectivity of 89% towards methanol proved that indeed, large particles of the PdZn alloy are needed to obtain methanol.

For the Zr(OH)<sub>4</sub> and ZrO<sub>2</sub> supported catalysts, a similar behaviour was observed: when using chloride, higher hydrocarbon selectivity was obtained and

Table 2  
Catalytic results on the CO hydrogenation ( $T_{\text{reaction}}$ : 320 °C)

Catalyst	Carbon selectivity (%) <sup>a</sup>								
	Activity <sup>b</sup>	CH <sub>4</sub>	C <sup>2+</sup>	CH <sub>3</sub> OH	DME	C2–C3-oxo	C4-oxo	Total oxo	CH <sub>3</sub> OH/DME
Pd(N)/ZnO	79	1.4	0.4	97.5	0.2	0.5(0.4 <sup>c</sup> )	0.0	98.2	487.5
Pd(C)/ZnO	65	62.1	7.9	29.9	0.0	0.0	0.0	29.9	∞
Pd(C)/ZnO <sup>d</sup>	41	7.5	3.9	88.6	0.0	0.0	0.0	88.6	∞
Pd(N)/ZrOH <sub>4</sub>	57	22.7	2.7	58.8	12.5	1.2(0.6 <sup>c</sup> )	2.0(1.4 <sup>e</sup> )	74.5	4.7
Pd(C)/ZrOH <sub>4</sub>	121	29.9	4.2	53.0	10.1	1.3	1.5(1.2 <sup>e</sup> )	65.9	5.2
Pd(N)/ZrO <sub>2</sub>	119	30.5	6.4	51.2	7.6	1.3	3 <sup>e</sup>	63.1	6.7
Pd(C)/ZrO <sub>2</sub>	152	39.1	3.1	52.0	3.2	1.7(0.5 <sup>c</sup> )	0.9	57.8	16.3

<sup>a</sup> CO<sub>2</sub> free.

<sup>b</sup> Units: mol CO converted/(kg Pd h).

<sup>c</sup> Methyl formate.

<sup>d</sup> Sinterized.

<sup>e</sup> *iso*-C4.

always a smaller particle size were observed by RAMAN and XRD. On the other hand, as seen in Table 2, selectivity towards total oxygenated compounds was higher when using nitrate. The previous XRD results indicated that when using  $\text{Pd}(\text{NO}_3)_2$  as precursor, the palladium particle size was larger. Again particle size seems to play an important role on the catalytic performance, as it can be said that large particles favours oxygenated compounds and small particles favours hydrocarbon formation. It cannot be ruled out, however an effect of conversion on selectivity. A relationship between high conversion and hydrocarbon formation and low conversion and oxygenated formation can also be established.

On zirconia-supported catalysts, methanol formation was not very much affected with precursor salt. However, as a difference from the ZnO-supported catalysts, oxygenated compounds other than methanol (i.e. dimethylether, methyl formate and isobutanol) were obtained on zirconia-supported catalysts. All these products can be formed by the presence of sites introduced by the support.

The  $\text{CH}_3\text{OH}/\text{DME}$  ratio is an indication of the acidic properties of the catalysts. The presence of DME is an evidence of the presence of acid sites as it is well known that DME is produced via methanol dehydration. On the other hand, the presence of *iso*-butanol and methyl formate is evidence of the presence of basic sites. As seen from the  $\text{CH}_3\text{OH}/\text{DME}$  ratio, the order of acidity of the supports is:  $\text{Zr}(\text{OH})_4 > \text{ZrO}_2 \gg \text{ZnO}$  independently of the salt precursor used. Catalysts with higher values of  $\text{CH}_3\text{OH}/\text{DME}$  ratio have little or none acidic sites and, as a consequence, formation of mostly methanol and methyl formate is observed. On the contrary, the catalysts with both type of sites like  $\text{Pd}/\text{Zr}(\text{OH})_4$  and  $\text{Pd}/\text{ZrO}_2$  (as evidenced by the lower  $\text{CH}_3\text{OH}/\text{DME}$  ratio and the presence of methyl formate) produced the higher amount of higher oxygenated. On the other hand, the presence of *iso*-butanol indicates that the chain growth mechanism applying for oxygenated compounds seems to be aldolic condensation which would take place on basic sites. A double bifunctionality on the catalysts for the production of higher oxygenated seems evident. On the one hand, an acid–base bifunctionality of the support seems to be needed for the formation, stabilisation, chain growth and further reactivity of intermediates such as formate as well as for the dis-

sociative adsorption of CO, and on the other hand, a metal–support bifunctionality, where the palladium metal particles would play the role of hydrogenate the intermediates and possibly adsorb non-dissociatively the CO. An alternative explanation was given recently by Bell who reported [26] that on  $\text{Cu}/\text{ZrO}_2$  catalysts, methanol synthesis occurs via a bifunctional mechanism, where the  $\text{ZrO}_2$  adsorbs CO which is hydrogenated in the metal to methoxide groups. These methoxide groups are released from the  $\text{ZrO}_2$  surface via either hydrolysis or reductive elimination. He describes this process assuming that Cu serves to adsorb  $\text{H}_2$  dissociatively and provide atomic hydrogen to the  $\text{ZrO}_2$  via spillover. The role of the  $\text{ZrO}_2$  support is described in terms of its amphoteric characteristic. The Lewis acid centres contribute to the formation of carbonate species whereas the hydroxyl groups are involved in the formation of bicarbonate and formate species.

A straight forward interpretation of our results is not easy, mainly because the many interacting effects involved. However, a clear influence of particle size and the acid–basic properties of the support were evidenced. The nature of the precursor salt has an indirect effect on the catalytic properties of the systems, as it seems to influence the particle size which in turn is responsible for selectivity. ZnO and  $\text{ZrO}_2$  are known to be components of the low and high pressure methanol synthesis commercial catalysts. Furthermore,  $\text{ZrO}_2$  is in itself an *iso*-synthesis catalyst. The role of these supports in CO hydrogenation does not seem to be that of an inert support for palladium; instead they seem to play the role of co-catalysts.

#### 4. Conclusions

This investigation provides additional evidence that the selectivity and activity of supported palladium catalysts for the CO hydrogenation reaction depends on the nature of the salt precursor, particle size and on the acid–base properties of the support. From the analysis of our experimental data, the following conclusions may be drawn

1. In general, higher activities are obtained when using  $\text{PdCl}_2$  instead of  $\text{Pd}(\text{NO}_3)_2$ .

- The Pd(NO<sub>3</sub>)<sub>2</sub>/ZnO catalyst shown the highest methanol selectivity which was related to the presence of large particles of a PdZn alloy.
- The particle size was dramatically influenced by the salt precursor, PdCl<sub>2</sub> lead to smaller particles than Pd(NO<sub>3</sub>)<sub>2</sub>.
- Particle size seems to play an important role on the catalytic performance: large particles favours oxygenated compounds and small particles favours hydrocarbon formation.
- As seen from the CH<sub>3</sub>OH/DME ratio, the order of acidity of the supports is: Zr(OH)<sub>4</sub> > ZrO<sub>2</sub> > ZnO independently of the salt precursor used.
- Pd/ZrO<sub>2</sub> catalysts were more active than Pd/Zr(OH)<sub>4</sub> and Pd/ZnO catalysts.
- A double bifunctionality on the catalysts for the production of higher oxygenated seems evident. On the one hand, an acid–base bifunctionality of the support seems to be needed for the formation, stabilisation, chain growth and further reactivity of intermediates such as formate as well as for the dissociative adsorption of CO, and on the other hand, a metal-support bifunctionality, were the palladium metal particles would play the role of hydrogenating the intermediates and possibly adsorb non-dissociatively the CO.

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