A new method of direct synthesis of bimetallic phases: Silica supported Pd–Cu catalysts from mixed acetylacetonates

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Abstract

The direct synthesis on a silica support of well defined, crystalline, mixed Pd–Cu bis-acetylacetonates has been achieved and the structure of these new compounds was determined by powder X-ray diffraction. These clusters have been deposited on a silica support and their thermal decomposition under helium was followed by in situ X-ray diffraction, thermo-gravimetry and mass spectroscopy. Microcrystalline metallic alloys with a narrow distribution of composition and particle size in the 2–4 nm range are obtained. Infrared experiments of CO chemisorption confirm the homogeneity of composition of the particles but conclude to a partial coverage of palladium by copper.

1. Introduction

An interest for the Pd–Cu bimetallic catalysts studied here is the expected (and already known) improvement for selective partial hydrogenation reactions of polyolefins or alkynes [1]. But to reach the requested goal of a very high selectivity without too large reduction of activity, the surface of the Pd particles has to be *partially* but *uniformly* covered by Cu and overall no pure Pd particles should remain on the support.

Most of the methods used to prepare bimetallic catalysts are based on co-impregnation, successive impregnations or co-exchange with the salts of the two metals [2,3]. This was the case

for example of the Pd–Cu/SiO$_2$ catalysts prepared by Leon y Leon and Vannice [4–6] and of the Pd–Cu/Al$_2$O$_3$ studied by Furlong et al. [7].

If in many cases EXAFS and X-ray diffraction show that to some extent alloys are formed, a careful observation by analytical microscopy of individual particles, when performed, also shows that these methods of preparation rarely lead to particles with a homogeneous composition. The reasons for this lack of homogeneity are related to difference of interaction strength between the support and the two precursors and to differences of reducibility of the two cations. This phenomenon was observed in a recent example in which silica supported Pd–Ni catalysts were prepared by co-exchange with Pd(NH$_3$)$_4$(OH)$_2$ and Ni(NO$_3$)$_2$6H$_2$O [8]. In this typical case, analytical microscopy performed on individual particles showed that they have a

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large dispersion in composition. An alternative way to prepare the same catalysts, described in the same paper, consists in grafting an organometallic compound of nickel on pre-reduced Pd particles. In that case, the observed deviation with respect to the mean composition was strongly reduced.

The leading idea of the present work is different: one tries the direct synthesis on the support of well defined compounds containing both metals in defined proportion, in a large Pd/Cu range and to further eliminate the organic ligands. Bis(2,4-pentanedionato)Pd(II) and Cu(II) were used in so far as original material to synthesize mixed Pd–Cu compounds.

2. Experimental

2.1. X-ray diffraction and electron microscopy

The crystallization on the support of the organometallic compounds and the formation of the metallic phases were followed by powder X-ray diffraction using two instruments. For the study of the deposition of the precursors, a classical Philips diffractometer equipped with a graphite monochromator placed before the scintillation detector, was sufficient. The silica background was subtracted with the DIFFRAC-AT program package. To study the formation of the alloys, which needs a heating under controlled atmosphere, an oven which can be flowed by various gases mounted on a D500 Siemens goniometer equipped with a position sensitive detector (Raytech), was preferred [8].

The granulometry of the particles was determined with a JEOL 100 CX electron microscope with the observation of 1000 particles; surface and volume averaged mean diameters were determined using the classical expressions:

$$d_S = \sum n_i d_i^3 / \sum n_i d_i^2 \text{ and}$$

$$d_V = \sum n_i d_i^4 / \sum n_i d_i^3$$

The homogeneity of composition of individual particles was determined with a VG HB 501

analytical microscope by measuring with a Si–Li detector the intensity of the Lα and Kα emissions of Pd and Cu at 2.84 and 8.04 keV, respectively. The analysis of the smallest particles can be achieved by reducing the size of the probed area to 1 nm^2. A mean composition X_M was evaluated from the expression:

$$X_M = \sum X_i n_i d_i^3 / \sum n_i d_i^3$$

As shown in a recent study by this technique of the Pd–Pt system [9], the statistical error on the measurement is of the order of 10%, both because of the small number of atoms hit by the focused electron beam and by the limitation of the time of measurement. It was also shown that increasing the time of analysis on the same particle can produce a preferential sputtering of the most volatile metal, specially if it is located at the surface of the particles.

2.2. Thermal methods

The decomposition of the organo–metallic precursors was also followed by TDA-TG analysis with a SETARAM 92 instrument. The masses corresponding to H_2, CO_2, H_2O, CH_3CO^+ and CH_3COCH_3 were also simultaneously analyzed by mass spectroscopy.

The sample (15–20 mg) was introduced into the thermo-gravimetric apparatus to measure the temperature of the ligand elimination during the heating under helium. In a second experiment, the reduction under a mixture $N_2 + 1\%H_2$ was also followed. The temperature was raised from 370 to 870 K at a 10°/min rate. Between treatments, the samples were flowed with dry N_2 at 300 K during 1 h.

2.3. Infrared spectroscopy

Infrared was used both to follow the elimination of the organic ligands and to study the chemisorption of CO on the reduced catalysts. A Brucker IFS 110 FT instrument working in absorption mode was used. The wafer was introduced in a quartz cell closed by CaF_2 win-

dows and allowing evacuation and thermal treatments under gas flow.

3. Preparation

3.1. Synthesis of the silica supported mixed acetylacetonates

A first attempt was made to synthesize mixed crystals from the bis-acetylacetonates of the two metals (from Strem Chemicals). Fig. 1a shows the X-ray pattern of the $Pd(acac)_2$ powder after dissolution in toluene and recrystallization by slow evaporation of the solvent in a glass vessel at 350 K. The solid is better crystallized than the as purchased solid, but the positions and intensities of the X-ray lines are identical and correspond to the pattern calculated from the crystal structure data [10]. The pattern of the recrystallized $Cu(acac)_2$ shown in Fig. 1e is also in agreement with the literature [11]. If now a *mixture in well defined proportion of the solutions* of the two acacs is crystallized under the same conditions, the X-ray patterns are all different but correspond to pure phases. This can be seen on Fig. 1b and d, corresponding respectively to the $Pd_{80}Cu_{20}$ and $Pd_{40}Cu_{60}$ mixture. They all form well crystallized compounds with a crystal size of 50 to 100 nm, as estimated from the diffraction line width. Thus *new mixed compound have been synthesized* whose spectra have been indexed in the monoclinic lattice and the $P2_1/n$ (14) space group, the same group as that of $Pd(acac)_2$ and $Cu(acac)_2$. Therefore, the mixed compounds are composed of $Pd(C_5O_2H_7)_2$ and $Cu(C_5O_2H_7)_2$ molecules (two by uc) randomly distributed in the crystallographic sites. The unit cell parameters determined from these diffractograms are listed in Table 1.

The next step consists in the deposition of these precursors on a Degussa Aerosil 200 silica. To prepare Pd or Cu monometallic catalysts, the desired amounts of Cu $(C_5H_7O_2)_2$ or Pd $(C_5H_7O_2)_2$ dissolved in 300 ml of toluene are added to five grams of SiO_2 with stirring for
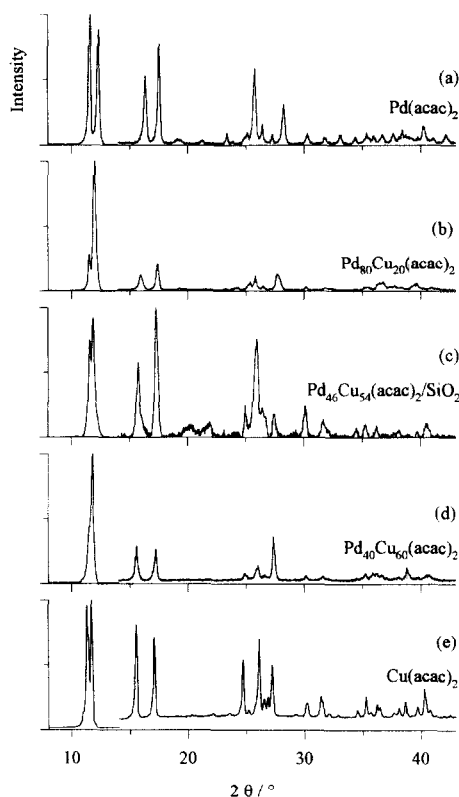

Fig. 1. X-ray patterns of the pure and mixed bis-acetylacetonates crystallized from toluene solutions: (a) and (b) unsupported $Pd(acac)_2$ and $Pd_{80}Cu_{20}(acac)_2$, respectively; (c) $Pd_{46}Cu_{54}(acac)_2 /SiO_2$; (d) and (e) unsupported $Pd_{40}Cu_{60}(acac)_2$ and $Cu(acac)_2$, respectively. The intensities for 2-theta angles higher than 14° are multiplied by 4.

24 h at room temperature. The mixture is filtered under vacuum and dried at 350 K for 15 h. The same procedure is employed to prepare the precursors of the bimetallic catalysts. Actually, to reach a given Pd/Cu ratio, it was necessary to start with solutions containing an excess of 30% of $Pd(acac)_2$.

When the crystallization is carried out on the silica support, following the procedure described above, limiting the amount of precursors to obtain a final metal concentration of 4 to 5%, the spectra (Fig. 1c) are identical to those obtained above, by direct crystallization in a glass vessel; only the intensities of the diffraction lines are modified probably because silica leads to a preferential development of particular planes.

Table 1
Unit cell parameters of the pure and mixed bis-acetylacetonates

Sample	a (nm)	b (nm)	c (nm)	β (°)	V (nm^3)
Pd(acac)$_2$ [a]	1.0835	0.5148	1.0125	93.3	0.5638
Pd(acac)$_2$ recrystallized	1.0855	0.5136	1.0120	93.3	0.5632
Pd(acac)$_2$/SiO$_2$	1.086	0.518	1.009	93.2	0.5661
Pd$_{80}$Cu$_{20}$(acac)$_2$ recrystallized	1.1121	0.5028	1.0229	92.7	0.5713
Pd$_{46}$Cu$_{54}$(acac)$_2$/SiO$_2$	1.125	0.497	1.027	91.9	0.5740
Pd$_{40}$Cu$_{60}$(acac)$_2$ recrystallized	1.1297	0.4809	1.0261	91.5	0.5573
Pd$_{31}$Cu$_{69}$(acac)$_2$/SiO$_2$	1.140	0.478	1.035	91.6	0.5630
Pd$_{24}$Cu$_{76}$(acac)$_2$/SiO$_2$	1.139	0.476	1.034	91.6	0.5600
Cu(acac)$_2$/SiO$_2$	1.142	0.473	1.038	91.9	0.5608
Cu(acac)$_2$ recrystallized	1.1401	0.4732	1.0371	91.9	0.5592
Cu(acac)$_2$ [a]	1.1331	0.4697	1.0290	91.84	0.5474

[a] From Refs. [10,11], respectively.

The interaction between the acetylacetonate crystals and the support is strong because of the multiplicity of hydrogen bonds which are formed with the hydroxyl groups of the silica. The reaction can be written in the following way [12]:

$$\equiv Si–OH + M(acac)_2$$
$$\rightarrow \equiv Si–O–Macac + acacH \quad M = Pd \text{ or } Cu$$
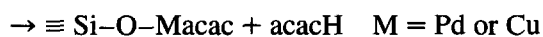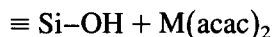
This scheme postulates that the fixation of the complex occurs by a ligand exchange with the surface hydroxyl groups.

3.2. Formation of the bimetallic catalysts

The decomposition of the organometallic precursors was studied by thermal gravimetric analysis coupled with mass spectrometry (TGA/MS). Fig. 2 shows the TGA curve obtained during the heating under argon of a sample containing 31 Pd at% (2.07 Pd wt%). The
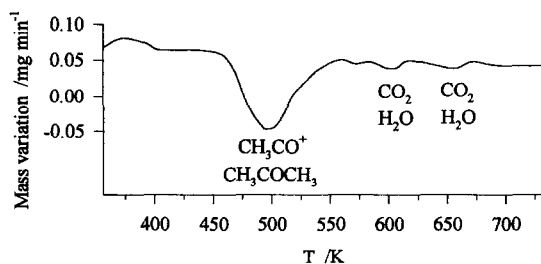
most important weight loss occurs between 470 and 570 K. From the mass spectrum shown on Fig. 3, it is ascribed to the elimination of the acetylacetonates ligands which break down into CH_3COCH_3 and CH_3CO^+ species. Moreover, from 470 to 620 K the elimination of H_2O and CO_2 is observed. Above 650 K, no further weight decrease is observed.

A treatment under hydrogen was also performed on samples first decomposed under Ar at 870 K. During the heat treatment, no weight variation and *no H_2 consumption* were detected. So, one can assume that the decomposition under Ar has indeed led to reduced metal. In this way, a reduction step is not necessary.
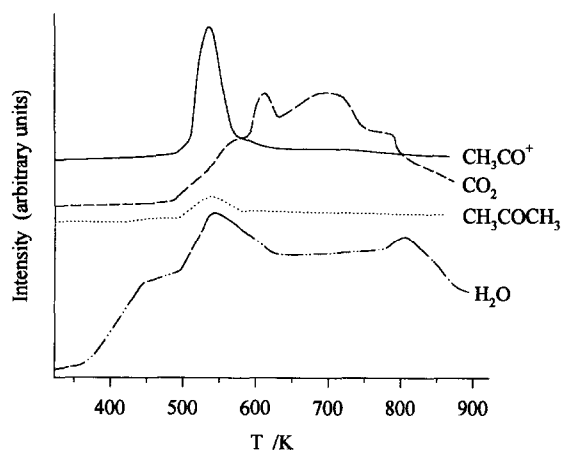

Fig. 2. Thermo-gravimetric analysis of the decomposition of the Pd$_{31}$Cu$_{69}$(acac)$_2$/SiO$_2$ sample.

Fig. 3. Mass spectroscopy analysis during the decomposition of the Pd$_{31}$Cu$_{69}$(acac)$_2$/SiO$_2$ sample: from top to bottom masses 43 (CH$_3$CO$^+$), 44 (CO$_2$), 58 (CH$_3$COCH$_3$), and 18 (H$_2$O).

Generally, in the preparation of metallic supported catalysts, the precursors are decomposed by heating in an oxidizing atmosphere. This treatment leads to the formation of oxides, requiring a subsequent reduction by hydrogen. In the present case, it is observed on the diffractograms of Fig. 4a, that the decomposition of the palladium acetylacetonates by heating under helium directly leads to metallic palladium at 470 K, corroborating the results of thermal analysis. Finally, little particle size increase occurs upon heating at 670 K. Metallic copper as well is obtained at 670 K (Fig. 4b), but exposure to air partly oxidizes the metal as shown by Fig. 4c. It is probable that the elimination of the acac moieties proceeds via a reaction with OH groups of the silica.

Concerning the three bimetallic systems, the X-ray spectra of Fig. 5 show that the situation is different for the extreme compositions, $Pd_{83}Cu_{17}$ and $Pd_{31}Cu_{69}$ on one hand and $Pd_{46}Cu_{54}$ on the other. Whereas the first two catalysts lead to fcc phases with well distinguishable (200) lines, for

Fig. 5. X-ray patterns of the 3 silica supported alloys $Pd_{83}Cu_{17}$, $Pd_{46}Cu_{54}$, and $Pd_{31}Cu_{69}$. Vertical bars indicate the position of the Bragg peaks for Pd (full lines) and Cu (dashed lines).

the 46/54 composition a bcc structure is observed coexisting with a small amount of fcc phase. This is exactly what is described in the case of bulk alloys in Refs. [13,14] which conclude that a fcc disordered α-phase is present in the whole composition range, except in the 36–45 Pd at% composition domain where a ordered bcc structure called β-phase (isotypic with CsCl) can be obtained.

As can be seen from Table 2, the surface and volume weighted diameters are close, confirming that the metallic particles have a uniform diameter ranging from 2 to 4 nm (Fig. 6). This size, which corresponds to particles of 100 to 1000 atoms of metal, is the indication that little coalescence has occurred on the support during the elimination of the organic ligands. The composition of the particles measured by analytical microscopy is slightly different from the value measured by chemical analysis (CA). Especially, one always finds a larger Pd concentration on the Cu rich samples. This can be ascribed to a probable *preferential sputtering of copper* by the focused electron beam during the EDX analysis because this element is expected
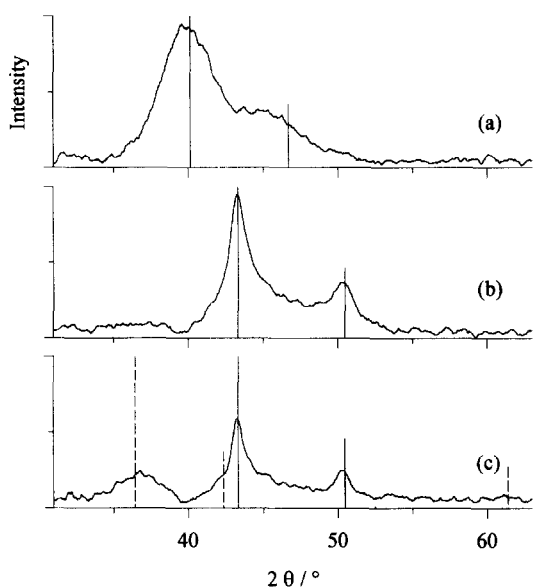

Fig. 4. X-ray patterns obtained upon heating the precursors: (a) at 470 K pure Pd; (b) at 670 K pure Cu; (c) Cu after exposure to air at room temperature. Vertical bars indicate the position of the Bragg peaks for Pd (pattern (a), Cu (patterns (b) and (c) full lines) and Cu_2O cuprite (pattern (c) dashed lines) extracted from the powder diffraction file.
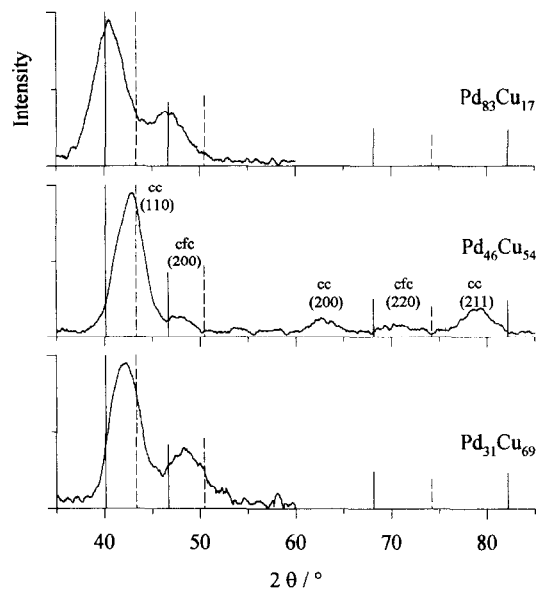
Table 2
Composition of the bimetallic catalysts

Sample	Composition (wt%)		Composition Pd (at%)			Mean diameters [a] (nm)	
	Pd	Cu	CA	STEM	XRD [b]	D_S	D_V
$Pd_{83}Cu_{17}/SiO_2$	4.1	0.5	83	88	81	2.8	3.1
$Pd_{46}Cu_{54}/SiO_2$	2.3	1.6	46	55	44–48 [c]	3.1	3.3
$Pd_{31}Cu_{69}/SiO_2$	2.1	2.8	31	50	25	3.3	3.6

[a] D_S is the mean diameter determined by X-ray line broadening. D_V is measured by electron microscopy.
[b] Composition calculated from the position of the (111) diffraction line.
[c] The first figure is the composition of the bcc phase, the second of the fcc.

to be located at the surface and because the heat elimination is limited on an oxide support. This hypothesis of systematic deviation of the composition measured by EDX-STEM is corroborated by the comparison between TEM and X-ray diffraction. First, the diameters measured by the diffraction line-width agree with the diameter measured by electron microscopy. Indeed, a broad distribution of composition would lead to wider lines and to smaller diameters than the values measured by TEM. Secondly, the mean composition determined from the unit cell parameter is in good agreement with that obtained from the chemical analysis.

3.3. Infrared study of the CO chemisorption

The experiments of CO adsorption were performed on samples treated under argon at 770 K in the infrared cell and cooled down to 280 K. 10 Torr of CO was then introduced before evacuation at 280 K, to leave only the irreversibly adsorbed fraction of this adsorbate. As
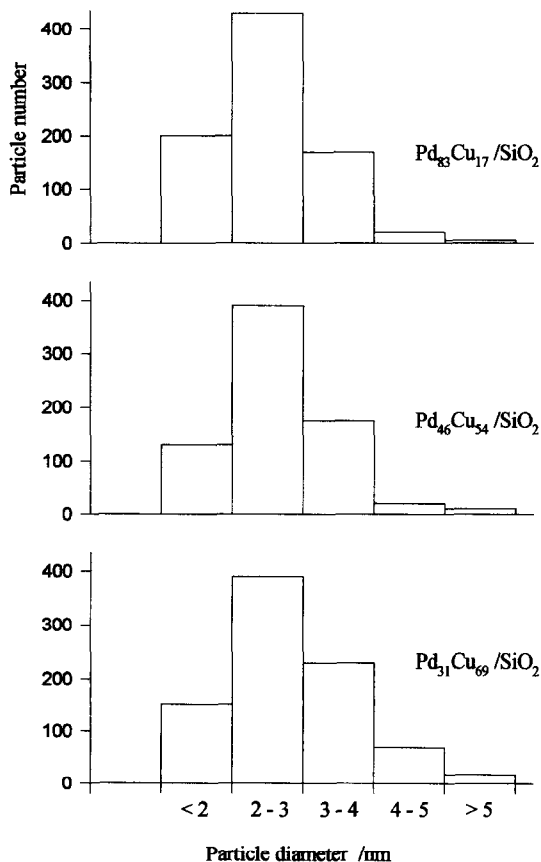
Fig. 6. Number distributions of the diameters of the particles for the 3 silica supported alloys $Pd_{83}Cu_{17}$, $Pd_{46}Cu_{54}$, and $Pd_{31}Cu_{69}$.
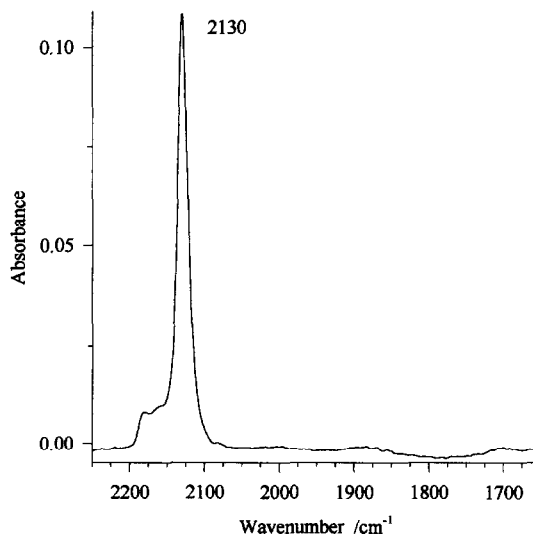
Fig. 7. IR spectrum of CO chemisorbed on Cu/SiO_2. The absorbance is given per mg of copper.

can be seen on Fig. 7, only one νCO mode is observed on Cu/SiO$_2$ located at 2130 cm^{-1}. It is uneasy to decide from other works [15–17] whether this frequency corresponds to CO adsorbed on metallic Cu ($\nu = 2110$–2120 cm^{-1}), on Cu$_2$O (2120 cm^{-1}) or on CuO (2140 cm^{-1}).

The IR chemisorption of CO on Pd has been studied by a very large number of authors as well on single crystals with various orientations as on small particles. The spectrum shown in Fig. 8 for Pd/SiO$_2$ is similar to those obtained by others [18]: the 2075 cm^{-1} mode, also present on all single crystal faces, is always assigned to a on-top adsorption.

The complex structure extending from 1830 to 1980 cm^{-1} is assigned from combined LEED and IR experiments on single crystal faces, to multibonded species. However, their frequencies are highly coverage dependent. For example, in the case of chemisorption on a (100) surface, Ortega et al. [19] have shown that the molecule adsorbed at 300 K is bridge bonded with a frequency of vibration shifting from 1900 to 1980 cm^{-1} when the coverage increases from 0.1 to 0.6. At the same time, the adsorption energy decreases from 150 to 70 kJ mol^{-1}.

Considering our experimental procedure, the coverage of our supported catalyst is probably

Fig. 8. IR spectra of CO chemisorbed on Pd/SiO$_2$ and on the supported alloys. The absorbance is given per mg of palladium.

close to 0.5–0.6 and the band we have observed at 1975 cm^{-1} has a frequency close to that on (100) faces. But this frequency, attributed to bridge bonded molecules, has also been observed at high coverage by the same authors on more open faces like the (210). Such surfaces constitute good models for the crystallites with edges where the Pd atoms have a strong reduction of their coordination number. The mode located at 1925 cm^{-1} would also correspond to a bridge bonded molecule but on (111) facets; indeed, Kuhn et al. [20] found that, on this face, the 3-fold hollow sites are occupied below 200 K, together with on top sites (1850–1880 and 2100 cm^{-1}). But at higher temperature, the molecules move to bridge sites, with a frequency of 1920–1940 cm^{-1}. A mode at the same frequency is measured on (110) faces by Raval et al. [21].

On the Pd$_{83}$Cu$_{17}$ alloy (Fig. 8), a strong increase of the transmittance in the 1800–2200 cm^{-1} region is observed, indicating a diminution of the coverage. The bands located at 1925 and 2075 cm^{-1} are still observable with a reduced intensity, but the 1975 cm^{-1} mode is totally suppressed. The suppression of this mode is probably the indication that the Cu atoms are preferentially located on the *edges of the small crystals* and (or) on the (100) open faces, rather than on the (111) facets. This idea of preferential migration of Cu on low coordination sites is supported by a recent theoretical study of the surface segregation in Pd–Cu single crystals [22]. Indeed, the Cu concentration of a (100) face of a Pd$_{50}$–Cu$_{50}$ alloy is 90%, whereas it is only 55% on a (111) surface, in agreement with the experimental value obtained from ion scattering spectroscopy [23]. The same theory concludes that edges are even more populated by Cu atoms than the (100) faces.

A still more convincing argument concerning the location of the Cu atoms on well defined sites is the Monte Carlo simulation, based on the tight binding approximation, recently performed [24] on the same Pd$_{83}$Cu$_{17}$ aggregates. It was found that for a 586 atoms cubo–oc-
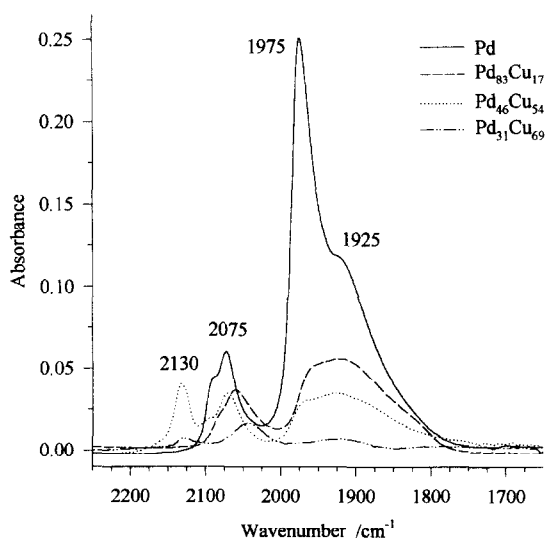
tahedral cluster, which has roughly the same diameter as our particles, 32% of the surface sites are covered by Cu and moreover, this proportion reaches 72% for corner and edge sites. A cross verification of the validity of these MC predictions is the perfect agreement between the mean surface concentration found by the simulation and the measurement performed by low energy ion scattering, leading to a Cu concentration of 29%. Obviously, such a coverage of the edges by Cu would totally suppress the sites available for bridge bonding.

On the alloys which have a larger Cu concentration (Fig. 8), the same features are qualitatively observed except that a band at 2130 cm^{-1}, due to the adsorption on Cu, appears. Finally *no substantial shifts* of the $\nu C-O$ frequency is observed on the alloys, discarding a strong electronic effect of Cu on Pd.

4. Discussion

To come back to the differences of properties which can be attributed to the method of preparation, let us consider the chemisorption of CO studied in Ref. [5]. These authors, using a co-impregnation by salts of the two metals to prepare their catalysts, observed a linear decrease of the volume of adsorbed CO with the Cu content, the uptake being reduced only by 25% for a Cu concentration of 40 at%. Actually, the solids behave as if they were composed of pure Pd and Cu particles. On the contrary, if one compares now the IR spectra of Fig. 8 for CO adsorbed on the pure Pd and on the $Pd_{83}Cu_{17}$ catalysts respectively, the reduction of intensity is already larger than 50%. If the homogeneity of composition was identical for the two types of samples, one would have found a comparable reduction of CO uptake for a similar composition and temperature of preparation, 670 K. In other words, the preparation method using these mixed complexes leads to a more uniform composition of the active surface with a larger copper segregation.

Conversely, the method used by Furlong et al. [7], using the impregnation of a Pd catalyst by Cu acetate, certainly leads to rather homogeneous particles. Indeed, these authors observed a steep non linear decrease of the hydrogen adsorption capacity: the sample with the $Pd_{80}Cu_{20}$ atomic composition chemisorbs 1/3 of the amount fixed on pure Pd.

A future work will aim at measuring the actual surface composition and the catalytic properties.

5. Conclusion

New Pd–Cu molecular compounds have been synthesized and identified by X-ray diffraction. These mixed bis-acetylacetonates complexes are under the form of small crystals (50–100 nm), strongly adsorbed by hydrogen bonding to the OH groups of the silica support. A simple heating under rare gas leads to metallic alloys, with a particle size of 2–4 nm and rather uniform composition. Infrared spectroscopy studies of CO chemisorbed on these alloys show that the Cu atoms are probably located at the surface and have a strong tendency to occupy the edge sites and (100) facets of the particles. Additional experiments are now needed to sustain this hypothesis of surface segregation of copper. Also, measurements of the reactivity of these catalysts have to be carried out to compare their performances with those prepared in a different way by the authors of Refs. [4,7].

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