Surface and Bulk Characterisation of Metallic Phases Present during CO Hydrogenation over Pd−Cu/KL Zeolite Catalysts

James A. Anderson,* Marcos Fernández-García,† and Gary L. Haller‡

*Royal Society Research Fellow, Department of Chemistry, The University, Dundee DD1 4HN, Scotland, United Kingdom; †Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco, 28049 Madrid, Spain; and ‡Department of Chemical Engineering, Yale University, New Haven, Connecticut 06511

A series of Pd−Cu/KL zeolites with varying Pd : Cu ratios have been studied by a combination of FTIR and XANES. XANES indicates that only one PdCu alloy is formed for all samples and that the bulk of the alloy is not modified by extended periods under CO/H$_2$ at elevated temperatures. A combination of low temperature adsorption studies and *in situ* high temperature/high pressure FTIR indicates that an adsorbate induced surface segregation of Pd occurs following exposure of the bimetallic catalysts to a CO/H$_2$ reaction mixture under hydrogenation conditions. A progressive loss in Pd three-fold adsorption centres is observed as a function of time in contact with the reaction mixture.   © 1996 Academic Press, Inc.

INTRODUCTION

The ability to determine the state of a catalyst surface under actual operating conditions remains of great importance in this field of science. Many techniques are available which may give a detailed surface characterisation of the materials at ambient temperature, but in order to relate this data to activity/selectivity measurements obtained under working conditions it must be assumed that no modifications occur under high temperature/high pressure conditions. This can be an unjustified assumption as it is known that sintering, poisoning, or coking may occur, leading to a change in metal area or morphology and average coordination number. Interaction between adsorbate and adsorbent may lead to particle modification or disruption at room temperature for monometallic (1) and bimetallic catalysts (2). An additional possibility in the case of bimetallic catalysts is that reagents under reaction conditions may induce a segregation of one component leading to an enhanced concentration at the surface. Infrared spectroscopy remains one of the few available techniques to be able to provide detailed information on the catalyst surface under working conditions. This is particularly true when one of the reagents is CO which has been well studied on metal surfaces in both single crystal and supported catalyst forms. However, an IR spectrum is an average of everything seen by the reagent molecule, and thus will not give detailed information on the distribution of components in a bimetallic catalysts unless the number of different metallic phases present is known with a degree of certainty.

We have recently combined a XANES-TPR and IR-CO study of Pd−Cu/KL zeolite to determine the influence of reduction temperature on the surface and bulk characteristics of these catalysts (3). Above 623 K, reduction gave rise to a series of substitutionally disordered alloys with electronic modification of both components and giving formal compositions Pd$_{33}$Cu$_{67}$, Pd$_{50}$Cu$_{50}$, and Pd$_{67}$Cu$_{33}$. The Pd−Cu system is well known to favour segregation of copper (4) with the strain energy playing a significant contribution due to the relatively large difference in atomic radii of Cu and Pd (5). The (100) and other open surfaces show a greater Cu segregation than the (111) close packed surface with the latter showing only around 5% enrichment (5). In the case of small bimetallic clusters, a surface segregation of Pd has been claimed to account for experimental results (6).

Supported Pd−Cu catalysts have been studied for a number of reactions including CO and alkene oxidation (7, 8), CO, benzene and toluene hydrogenation (9, 10), and ethanol decomposition (10). The distribution of Cu within the bimetallic particle may affect catalytic behaviour according to the role of the copper and to the nature of the reaction being studied. Copper may play a role as an active phase, as an inert diluent, as a promoter, or in stabilising Pd against sintering. For reactions such as ethane hydrogenolysis where an ensemble of Pd atoms is required, surface dilution by Cu will have an adverse effect on activity whereas the TOF of Pd for methanation may be unaffected by Cu due to the structure insensitive nature of the reaction on this combination of metals (9). The influence of copper in the latter reaction may depend on the exact reaction mechanism since methanation proceded by CO dissociation requires ensembles of Ni atoms in Ni−Cu catalysts (11, 12) but may be less influenced by Cu if methanation proceeds via oxygen containing intermediates over Pd (13). On the other hand, the TOF of Pd for CO oxidation may be enhanced

by the presence of Cu due to an increase in surface oxygen concentration (7). In many cases, room temperature CO adsorption was used to characterise the surfaces of catalysts which were used at higher temperatures in reaction (7, 8, 10). Due to the higher adsorption enthalpy of CO on Pd (14) than Cu (15) a segregation of Pd may be envisaged although Pd–CO bonding is weaker in PdCu alloys than for pure Pd and the heat of adsorption of CO on Cu may increase by $23 \, \text{kJ} \, \text{mol}^{-1}$ in PdCu compared with pure Cu (4).

In the present study, we combine room temperature adsorption measurements with a high temperature/high pressure IR study of CO hydrogenation and a XANES study of the catalysts under CO/H_2 at elevated temperature to examine how the surface and bulk phases are influenced by reaction conditions.

EXPERIMENTAL

Three bimetallic catalysts containing 1% Pd and 1, 0.5, and 0.25% Cu and two monometallic reference catalysts containing 1% Pd and 1%Cu (labelled PdCu100, PdCu50, PdCu25, Pd100, and Cu100, respectively) were prepared by co-impregnating KL zeolite (Tosoh Corp., Japan) with the nitrate precursors at pH 8. Samples were dried overnight at 373 K and then calcined at 573 K for 2 h in a flow of oxygen (0.41/min g) at 573 K.

For IR measurements, pressed powder discs of 25 mm were prepared by compacting the loose powder at 1.5 tons between two polished stainless steel dies. Catalyst discs were heated in a flow (100 $\text{cm}^3 \, \text{min}^{-1}$) of 3.5% H_2 in Ar at 5 K min^{-1} to 623 or 773 K before maintaining this temperature for 30 min. The cell was purged in a flow of dry nitrogen for 30 min at reduction temperature followed by cooling to 573 K. The sample was then outgassed in dynamic vacuum for 5 min at 573 K before introduction of the CO/H_2 mixture (1:2) at a total pressure of 10 bar. IR spectra were recorded as a function of reaction time using a Perkin Elmer 1720X Fourier transform spectrometer operating at a resolution of 4 cm^{-1} and accumulating 25 scans for each spectrum. Other experimental details including the use of the high pressure IR cell in CO hydrogenation are as previously reported (16, 17). Spectra were recorded with the catalyst samples at the high pressure and temperature unless otherwise stated.

XANES spectra of the Cu K-edge were recorded at the National Synchrotron Light Source facility using a double-crystal Si(111) monochromator with an estimated resolution of 0.7 eV. Samples were measured in the transmission mode with nitrogen filled ionisation chambers. The samples were self supporting with an absorbance of 2 and the energy scale was calibrated by simultaneously measuring a Cu foil (absorbance 1.5) with the sample under study using a third ionisation chamber. The Pd K-edge was studied using the F-2 wiggler line at the Cornell High Energy

Synchrotron Source with a double crystal Si(220) at an estimated resolution of 1.4 eV. Experiments were conducted in the transmission mode using flowing Ar through the ionisation chambers. A Pd foil placed in a third ionisation chamber was simultaneously measured to provide calibration of the energy scale.

In both sets of experiments, samples were reduced for 30 min at 623 or 773 K in a flow of 5% H_2 in helium with the XANES spectra recorded in the presence of the gas mixture. Samples were cooled to reaction temperature (573 K) in the same gas before switching to a 1:2 CO/H_2 mixture at atmospheric pressure. Spectra were recorded at 10 min intervals over a period of 6 h.

RESULTS

Figure 1 displays IR spectra of the 623 K reduced catalysts following exposure to the reactants for 1 min. With the exception of Cu100, all samples display 2 bands in the 2000–1750-cm^{-1} region. Bands appear at ca. 1950 and ca. 1850 cm^{-1} for all Pd containing samples and can be
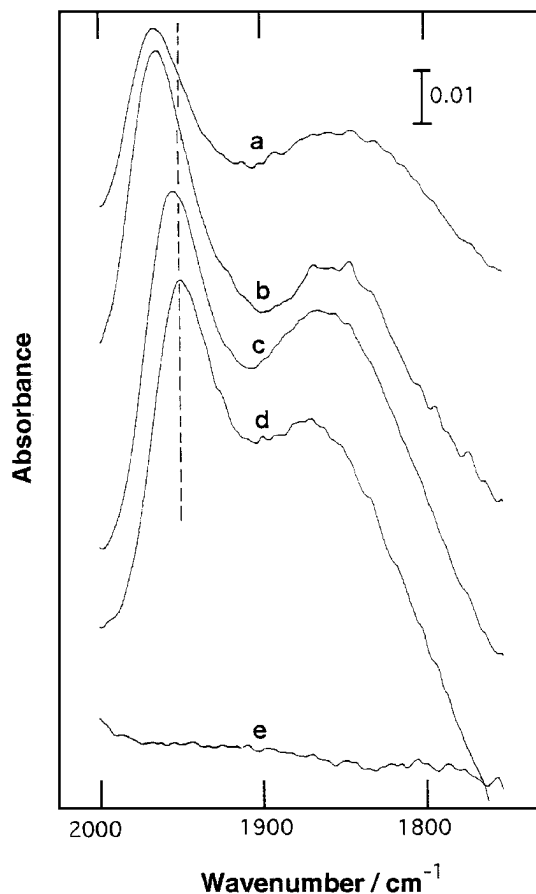

FIG. 1. IR spectra of (a) PdCu100, (b) PdCu50, (c) PdCu25, (d) Pd100, and (e) Cu100, reduced at 623 K and exposed to CO/H_2 (1:2) at 10 bar and 573 K for 1 min.

attributed to CO adsorbed at twofold bridging and three-fold hollow sites, respectively (18–22). An additional band at higher frequencies due to CO adsorbed in on-top mode was masked by bands due to CO gas under the high pressure conditions. The dotted line drawn indicates a wavenumber of 1950 cm^{-1}. It is clear that on decreasing the content of Cu there is a progressive shift to lower wavenumbers (1966, 1964, 1953, 1948 cm^{-1} in Figs. 1a–1d) of the band due to twofold bridging carbonyls. The band due to three-fold co-ordinated carbonyls was broader and less intense and the band maximum shifted to higher wavenumbers as the content of Cu was decreased (1847, 1854, 1858, and 1868 cm^{-1}).

Spectra for samples reduced at 773 K before exposure to the reaction mixture at 573 K show a similar series of trends although differing in fine detail. The exact band positions of the twofold bridging carbonyls were at lower frequencies than the bands in the corresponding samples after reduction at lower temperature (1965, 1954, 1949, and 1942 cm^{-1}).

The influence of reduction temperature and time in reaction on the frequency of the band due to twofold bridging carbonyls as a function of copper content, is shown in Fig. 2. The figure clearly indicates the shift to higher frequencies with increasing Cu loading but also that increasing time in reaction leads to a shift to higher frequencies. Higher reduction temperatures produced surfaces with lower frequency bridging carbonyls (Fig. 2).

In Fig. 3, spectra for the sample PdCu25 reduced at 773 K are compared for low pressure CO adsorption at ambient temperature (Fig. 3a) and in CO/H$_2$ (1 : 2) at 573 K (Figs. 3b and 3c). Apart from the exact position of the band due to twofold bridging carbonyls at 1980, 1949, and 1954 cm^{-1}, respectively, the most obvious difference between the spec-

FIG. 3. IR spectra of sample PdCu25 reduced at 773 K and exposed to (a) 20 Torr CO at 298 K, and 10 bar CO/H$_2$ (1 : 2) at 573 K for (b) 1 min and (c) 5 h.

tra is the non-appearance of a band due to threefold coordinated carbonyls for CO adsorbed at room temperature which appears as a broad band centred at ca. 1850 cm^{-1} in spectra recorded under reaction conditions.

The influence of exposure to reactants under reaction conditions for a catalyst with high copper loading is shown in Fig. 4. Unlike the sample after exposure to low CO pressures at ambient temperature where high surface copper concentration (3) prevents the formation of two and threefold coordinated carbonyls (Fig. 4a), the PdCu100 exhibits features at 1965 and ca. 1850 cm^{-1} attributed to these species (Fig. 4b). The intensity of the latter was less than in a comparable spectrum of a sample of lower Cu content (Fig. 3b) and after several hours in reaction the feature was no longer discernible (Fig. 4c). As observed for samples of lower Cu concentration (Figs. 2 and 3c) the band due to
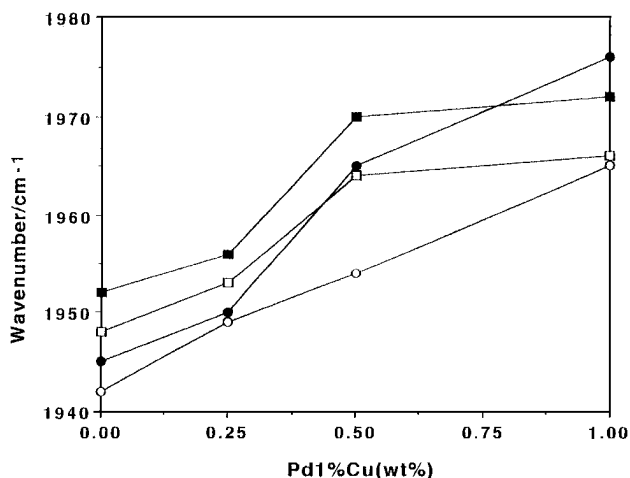

FIG. 2. Plot of band frequency for twofold bridging carbonyls as a function of copper content for samples in reaction at 573 K and in CO/H$_2$ (1 : 2) at 10 bar. Pd–Cu/KL samples reduced at 623 K and in reaction for 1 min (□) and 19 h (■) and for samples reduced at 773 K and in reaction for 1 min (○) and 19 h (●).
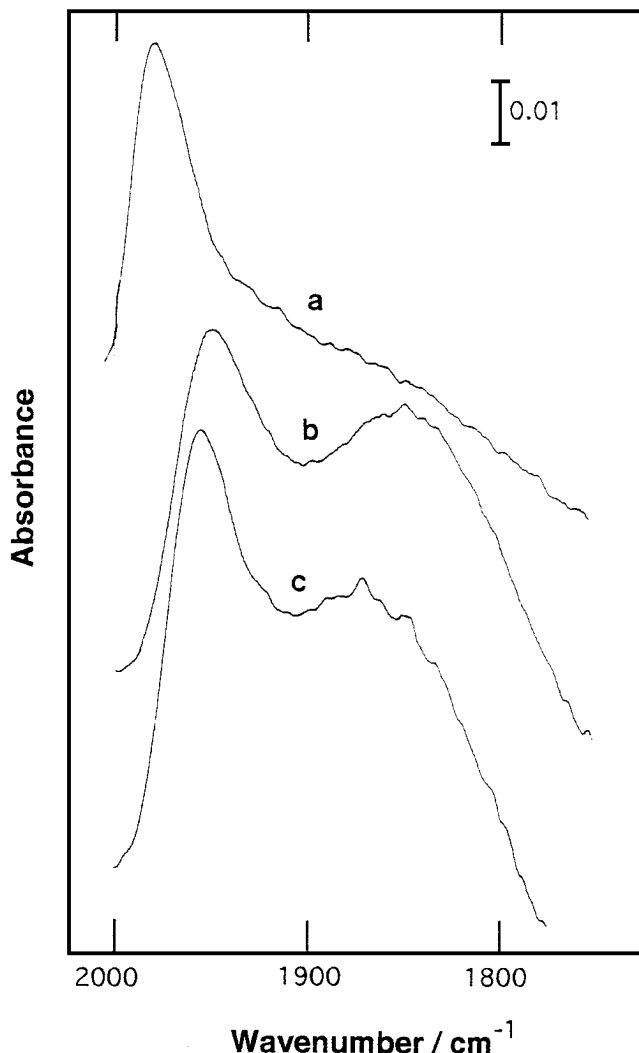
twofold bridging carbonyls was shifted to higher frequency as a function of time in reaction.

Figures 5 and 6 display XANES spectra for the monometallic and the representative PdCu100 sample at the Cu and Pd K-edges, respectively. Spectra are shown of the samples under an atmosphere of hydrogen at 623 K, and after 6 h exposure to a CO/H$_2$ mixture at 573 K. As detailed in a previous study (3), the bimetallic catalysts yield only one pure species after complete reduction ($T > 623$ K), indicating complete alloying of both components. The spectra show no appreciable changes induced by the reaction mixture at 573 K although minor changes in the electronic structure are observed in the Cu K-edge. The lack of experimental resolution at 23 KeV prevents a similar observation being made using the Pd K-edge.

As XANES indicate no particle disruption by the reaction mixture at elevated temperatures, experiments were conducted to ascertain the origin of the differences between surfaces in reaction and those observed by room tempera-
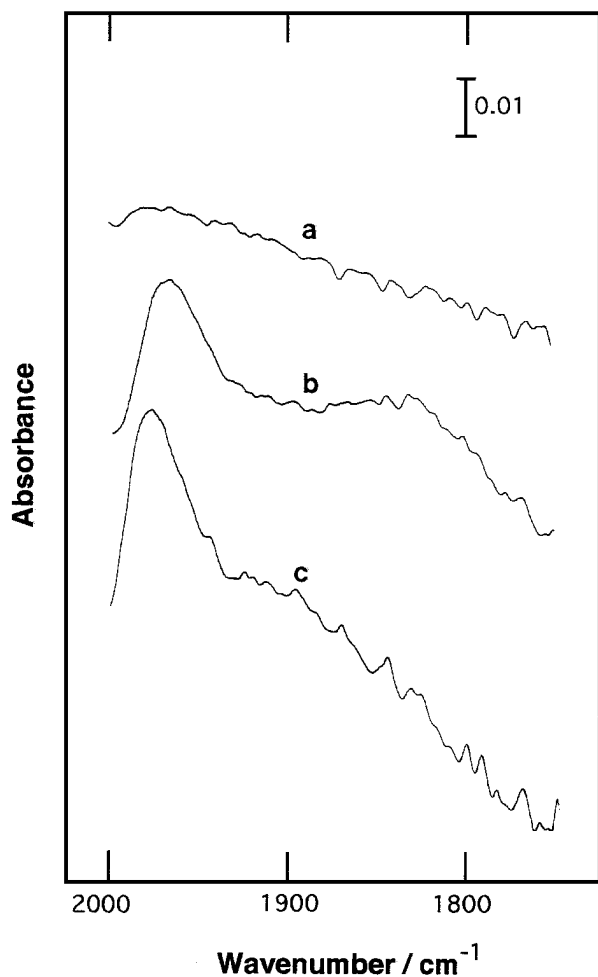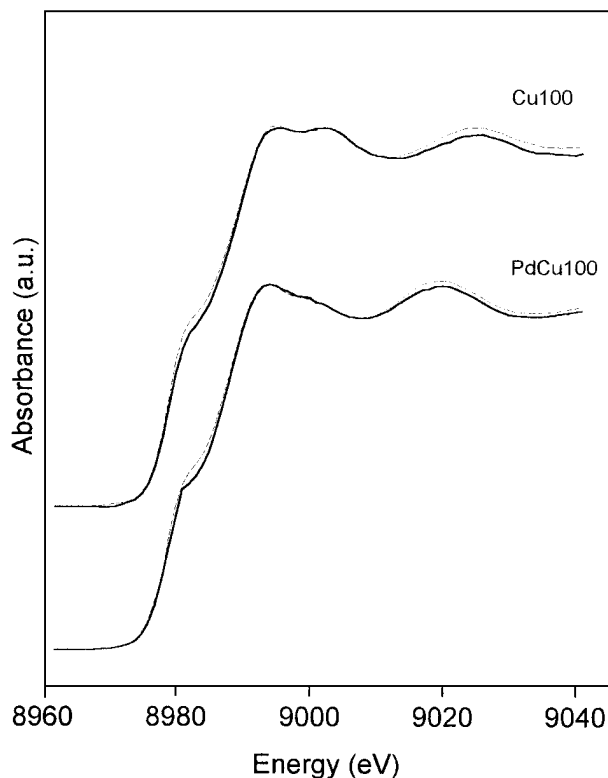

FIG. 5. XANES spectra of the Cu K-edge for the monometallic and PdCu100 bimetallic catalyst after reduction at 623 K (solid lines) and after reaction in CO/H$_2$ for 6 h at 573 K (broken lines).

ture adsorption studies. In Fig. 7 spectra are shown in the CO stretching region for the sample PdCu25 after reduction at 623 K and subsequent treatments in three different manners. In agreement with our earlier studies (3), adsorption of low CO pressures at 298 K leads to intense bands at 2065 and 1968 cm^{-1} due to linear and twofold bridging carbonyls, respectively (Fig. 7c). The former was not resolved in a spectrum of the sample under reaction conditions (10 bar at 573 K) due to intense gas phase CO bands, although maxima due to twofold (1953 cm^{-1}) and threefold (1862 cm^{-1}) coordinated carbonyls were clearly resolved (Fig. 7b). Both of these maxima (1975 and 1866 cm^{-1}) were also observed when low pressures of CO were exposed to the sample at 623 K followed by cooling to 298 K (Fig. 7a). This procedure also generated a surface with on-top adsorption sites as indicated by a less intense maximum at 2076 cm^{-1}.

DISCUSSION

One feature which distinguishes spectra recorded under reaction conditions from spectra for the same catalysts exposed to low pressures of CO at 298 K was the detection of two resolved bands due to CO adsorption on two- and threefold sites. Samples reduced at 623 and 773 K, and exposed to low CO pressures at 298 K displayed maxima
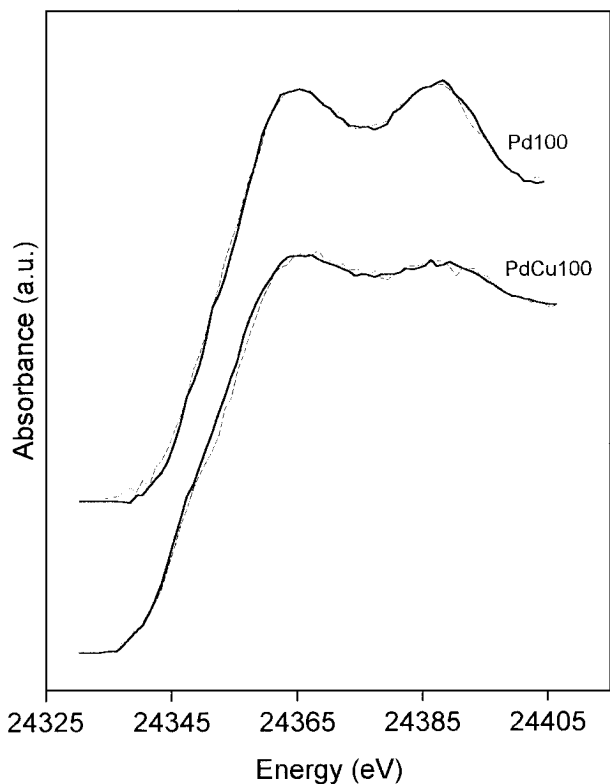

FIG. 4. IR spectra of sample PdCu100 reduced at 773 K and exposed to (a) 20 Torr CO at 298 K, and 10 bar CO/H$_2$ (1 : 2) at 573 K for (b) 1 min and (c) 5 h.

FIG. 6. XANES spectra of the Pd K-edge for the monometallic and PdCu100 bimetallic catalyst after reduction at 623 K (solid lines) and after reaction in CO/H$_2$ for 6 h at 573 K (broken lines).

XANES spectra obtained in the reaction mixture at the same temperature indicate that no disruption of the metal clusters occur at atmospheric pressure. All samples, both mono and bimetallic, show similar behaviour under CO/H$_2$, i.e., an increase in the density of unoccupied states (holes) at the Cu K-edge with respect to the reduced samples. One possible explanation is that this is related to the formation of CH$_x$ species at the surface as it is known that these species extract electrons from metallic clusters (25,26) and may significantly increase the number of 4p(Cu) empty states visible by XANES due to the small particle size expected for these catalysts. It is possible that a similar phenomenon is occurring for palladium but the instrument resolution and lifetime broadening severely limits the information available by XANES at the Pd K-edge. However, similar behaviour observed for Cu100, where hydrocarbon fragments are not expected in significant amounts, as for the PdCu catalysts, make this explanation unsatisfactory. An alternative explanation is that CO in the reaction mixture reacts with the support hydroxyls or K$^+$ ions, thus modifying the interactions at the Cu or PdCu support interface. Thermal treatment in CO is known to be more effective in removing suface hydroxyls from silica than other dry reagent gases (27). The formation of carbonate,
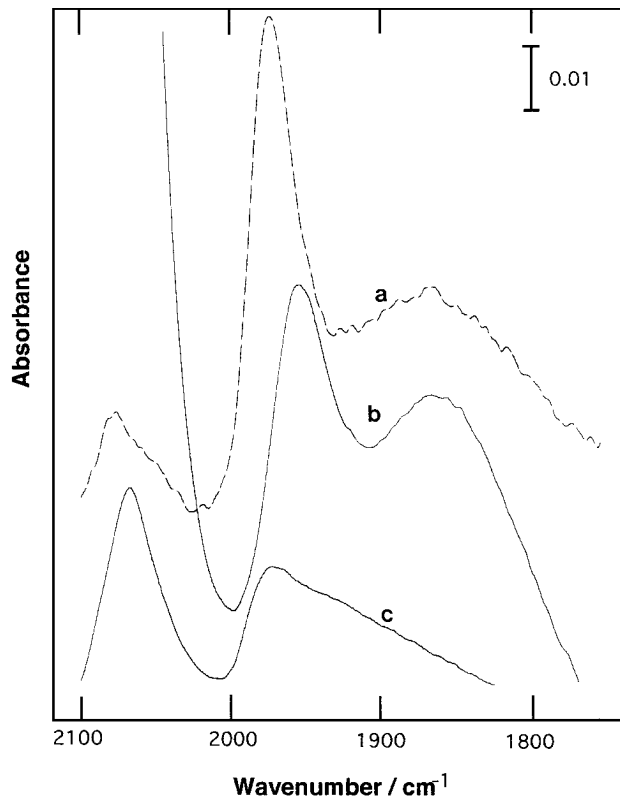
at ca. 1950 cm^{-1} with a broad tail to lower wavenumbers. Only Pd alone displayed resolved features under those conditions (3). The presence of surface copper in PdCu/KL (3) and PdCu/Al$_2$O$_3$ catalysts (7) results in a strong decrease in the amount of Pd atoms which can adsorb CO in the bridge form.

CO adsorption studies on Pd single crystal surfaces indicate the presence of on-top and threefold hollow sites for Pd(111) and of twofold bridging sites for Pd(100) (19, 20, 23). The progressive depletion of threefold bridging sites on increasing copper loadings for PdCu/KL catalysts while retaining on-top adsorption sites for Pd was interpreted (3) as an increase in surface copper concentration (geometric effect). This suppresion of multiple coordination can be rationalised in terms of ensemble statistics as first described by Soma-Nota and Sachtler using Pd–Ag (24). The ability to monitor the higher frequency region at low CO pressures and thus detect the presence of the linearly adsorbed CO, indicated that a single band due to bridging carbonyls did not infer a predominance of (100) faces. For higher Cu loadings both two- and threefold bridging sites were lost. Both of these adsorption modes were detected regardless of Cu loading for catalysts studied under reaction condition indicating the surface to be quite different from the one studied at room temperature.

FIG. 7. IR spectra of sample PdCu25 reduced at 623 K and exposed to (a) 20 Torr CO at 623 K, (b) 10 bar CO/H$_2$ (1 : 2) at 573 K, and (c) 20 Torr CO at 298 K.

carboxylate, and squarate type complexes derived from CO or CO_2 adsorption at the Cu/K^+ interface may be significant (28).

The relationship between carbonyl stretching frequency and copper content of the samples (Fig. 2) indicates that Pd is influenced by the other metal component in agreement with our previous results (3). Note that as a function of increasing CO coverage on the Pd(100) face, the band due to the C–O stretching mode of twofold bridging carbonyls moves to higher wavenumbers (20). If we assume that these carbonyls are dynamically decoupled from any Cu carbonyl, then a purely geometric dilution of Pd by Cu should result in a decrease in frequency with increasing copper content (29–31) as the dipole–dipole and vibrational coupling (i.e., through space and through substrate coupling) are diminished rather than the increase observed in Fig. 2.

It is unlikely that reaction products have a significant influence on the νCO of the twofold bridging carbonyl as the trend observed is similar for spectra recorded after 1 min or after 19 h (see below regarding the effect of reaction products on threefold bridging carbonyl adsorption sites). In general, the trends indicated in Fig. 2 suggest that all samples are equally effected by the period of reaction (another indication that reaction products are not responsible for the effects observed) and so the changes to the surface which lead to the differences between spectra recorded at room temperature and at elevated temperature and high pressure are induced by initial contact with the reaction mixture. The detection of a strong signal due to CO on threefold bridging sites indicates the presence of Pd(111) type patches which are not diluted by copper atoms. This indicates that the surfaces become enriched by Pd by exposure to CO/H_2 at high temperature and pressure. Spectra obtained by adsorption of CO at low pressures but at elevated temperatures (Fig. 7a) clearly indicate that this surface enrichment is due to an adsorbate enduced segregation of Pd to the surface. The segregation process significantly reduces the copper content of the surface leaving superficial Pd aggregates with (100) and (111) orientations corresponding to the two- and threefold coordinated carbonyls observed by IR.

For high copper loadings, the threefold bridging carbonyls become less abundant leaving a band due to CO which is twofold bridging. The inability under conditions of high CO pressure to monitor the linearly adsorbed CO, prevents an assignment to copper dilution of the Pd enriched surface or due to loss of (111) planes at the expense of (100) faces which would produce similar effects. The inversion of the intensity ratio linear : twofold bridging on going from adsorption of CO at 298 (Fig. 7c) to 623 K (Fig. 7a) may indicate that the Pd(100) face is preferentially exposed by the adsorbate induced segregation of Pd, as only a high Cu surface ratio would lead to the apparent depletion of ad-

sorption sites for the on-top adsorption of CO on Pd. The latter statement is clearly at odds with the detection of the intense twofold bridging band for the same sample and with the trends for results of low temperature CO adsorption as a function of Cu loading (3). The detection of the 1965 cm^{-1} band for PdCu100 in reaction and its extremely weak nature in the low temperature adsorption study (Fig. 4) would indicate that even at high copper loadings a surface enrichment in Pd occurs.

An additional point observed in the IR study conducted under reaction conditions is the progressive loss of Pd threefold centres as a function of time in reaction. This was observed regardless of reduction temperatures for all bimetallic catalysts but was particularly evident in the case of PdCu100 (Fig. 4c). The effect was observed for lower copper loaded samples after longer periods of time in reaction. A parallel decrease in signal to noise is detected in the Pd K-edge XANES spectra (Fig. 6) although not observed at the Cu K-edge (Fig. 5). This phenomenon may be explained by assuming that the Pd enriched surfaces undergo site blocking by strong adsorption of reaction products or coking or experience a progressive disordering process that mainly destroys the local order of the Pd(111) like patches. A loss of threefold hollow sites on Ni has been reported due to "C" deposition on Ni–Cu alloys (32). This process may be of significance in modifying catalytic selectivity given that atomic hydrogen is known to adsorb on three and fourfold hollow sites on Pd surfaces following dissociation (33). Such a scenario would result in a progressive decrease in surface hydrogen concentration as a function of reaction time.

As indicated in the Introduction, the distribution of Cu within the bimetallic particle may affect catalytic behaviour according to the exact role which the copper plays and to the nature of the reaction being studied. As CO adsorption at room temperature is often used to characterise these catalysts prior to use in reaction at higher temperatures or more forcing conditions, care must be taken in drawing conclusions regarding the influence of one metal on the other based on the distribution of components determined under non-reaction conditions. The present study clearly indicates that under CO hydrogenation conditions, surface enrichment in Pd occurs, thereby increasing the size of Pd ensembles relative to those present in the presence of low CO pressure at room temperature, and leading to a change in the bonding (from mainly linear to linear and bridging) of CO to the surface. Both of these modifications (geometric) are likely to change selectivity without even considering any possible influence of electronic effects. Additionally, the progressive loss of Pd threefold site as a function of time on stream may have a marked influence on selectivity over extended reaction periods. The importance of these findings in the mechanism and in the activity and selectivity of CO hydrogenation over Pd–Cu/KL catalysts will be reported (34).

ACKNOWLEDGMENTS

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