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The oxidation and scrambling of CO with oxygen at room temperature on Au/ZnO

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An FTIR and quadrupole mass study of CO adsorption and oxidation with $^{16}O_2$ and $^{18}O_2$ on Au/ZnO catalysts is presented. The experimental results indicate that: (i) CO is activated by gold in two molecular forms, a linear carbonyl species bonded at terrace Au sites and a carbonyl species bonded to Au peripheral sites; (ii) a band related to CO adsorbed on Au oxidized sites and a scrambling reaction between CO and $^{18}O_2$ indicate that oxygen is also activated on gold sites. The oxygen adsorbed on gold is probably strongly basic, as is the oxygen adsorbed on silver and on copper, and it can easily oxidize CO to CO_2.

Keywords: FTIR; CO adsorption; CO oxidation; CO scrambling; gold supported on ZnO; isotope exchange

1. Introduction

Pure gold has been considered for many years as almost catalytically inactive; however, recent works have clearly shown that gold is very active for the low temperature oxidation of CO when it is highly dispersed on a specific group of oxidic supports [1]. The activities observed are very sensitive to the preparation conditions, which noticeably affect the particle size of gold and the structure of the gold–metal oxide interface. On the basis of experimental results, mainly of kinetic, TPD and FTIR measurements, a four-step mechanism has been proposed for CO oxidation over supported gold: (i) adsorption of CO on metallic gold surface sites; (ii) oxygen adsorption, probably on metal oxide sites at the perimeter around gold particles; (iii) formation of carbonate-like species chemisorbed on the perimeter sites; (iv) decomposition of the carbonate-like species leading to CO_2 formation.

However, on ZnO the adsorbed carbonate-like species are usually stable up to 573 K [2]; therefore, it cannot be readily accounted for why the decomposition of these species could occur so easily on the gold modified oxides, leading to CO_2 formation at a temperature as low as 220 K. A Cu/ZnO catalyst prepared by calcination of coprecipitated carbonate showed a high activity of surface oxygen with CO already at 77 K [3,4]; it was proposed that this reactivity could be related to the high basicity of oxygen on copper. It can therefore be proposed that the oxidation of CO on Au/ZnO may also occur on the gold side of the Au–ZnO interfacial perimeter; however, up to now there is no experimental evidence supporting this hypothesis.

In order to clarify some aspects of the CO oxidation mechanism on gold modified zinc oxide and to try to obtain experimental evidence whether CO oxidation directly takes place on gold surface sites or not, combined FTIR and quadrupole mass experiments were undertaken with different $CO–O_2$ mixtures: $^{12}CO–^{16}O_2$, $^{12}CO–^{18}O_2$ and $^{12}CO/^{13}CO–^{16}O_2$. A full discussion of these results will be made in a next full paper [5]. Here, we will discuss mainly FTIR and quadrupole mass data evidencing the occurrence of a scrambling reaction of oxygen with CO molecules adsorbed on gold surface sites at room temperature. On ZnO, isotopic mixing in CO and oxygen exchange reactions were observed and studied at 573 K [6]. On the other hand, isotope exchange at 293 K between weakly adsorbed carbon monoxide molecules over Cu/ZnO catalysts was recently reported by Jackson [7]. A concerted mechanism between two or more adsorbed species was postulated.

Probably, exchange and scrambling reactions occur more often than we expect on the group IB elements, where CO is weakly adsorbed. A full understanding of these reactions can be relevant to obtain a complete comprehension of the mechanisms of CO oxidation or reduction to methanol on group IB elements and on sp metals, reactions in which the molecular integrity of CO is assumed [7,8].

2. Experimental

CO adsorption and oxidation experiments were undertaken on Au/ZnO powder (Au loading 5 at%) prepared by coprecipitation from $HAuCl_4$ and $Zn(NO_3)_2$ solution; the coprecipitated precursors were dried in vacuum at room temperature after washing and subsequently calcined in air at 673 K for 5 h.

Transmission electron microscopy was performed with a Hitachi H-9000 electron microscope operating at 300 kV.

The specific surface areas of the samples were obtained by a one-point BET method using a Quantasorb gas-flow type equipment (Quantachrome Corp.).

Catalytic activity measurements were carried out in a fixed bed reactor using 200 mg of catalysts of 90–120 mesh size. A standard gas containing 1 vol% CO in air was dried in a silica gel and P_2O_5 column and passed through the catalyst bed at a flow rate of 67 ml/min ($SV = 20\,000\ h^{-1}$ ml/g-cat.). For measurements performed at temperatures below 273 K, the reaction gas was additionally dried by a silica gel column maintained at 200 K.

The FTIR spectra were run with a Perkin-Elmer 1760 spectrometer, equipped with a MCT detector, at a spectral resolution of 2 cm^{-1}. During the experiments the pelletized samples were put in a quartz cell equipped with KBr windows, designed to treat the samples in situ, in controlled atmosphere.

The quadrupole mass spectra were taken by connecting the IR cell through a needle valve to a VG Micromass 100 instrument.

3. Results and discussion

Fig. 1 shows a nanometer resolution TEM photograph of the Au/ZnO sample. Gold particles are homogeneously deposited with a mean diameter of 5 ± 0.8 nm and were highly stable against electron beam during TEM observations.

The Au/ZnO sample exhibits markedly enhanced catalytic activity in CO oxidation, as clearly seen in fig. 2 by comparison with the catalytic activities of unsupported gold particles and ZnO powder. Since the specific surface areas of Au/ZnO

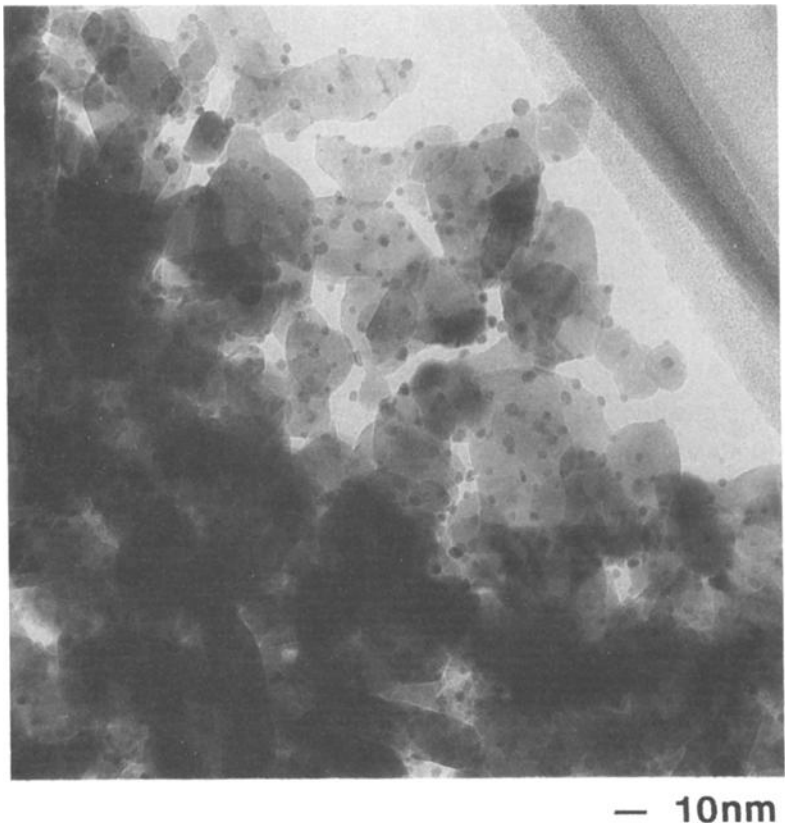


Fig. 1. TEM photograph of Au/ZnO prepared by coprecipitation followed by calcination in air at 673 K.

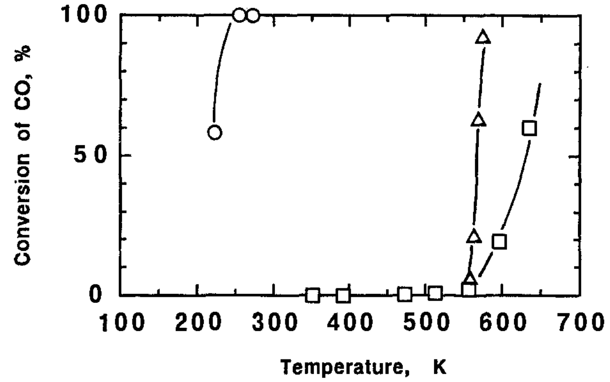


Fig. 2. Conversions of CO in catalytic oxidation as a function of catalyst temperature. CO 1 vol% in air, SV = 2×10^4 h^{-1} ml/g-cat. (○) Au/ZnO prepared by coprecipitation followed by calcination in air at 673 K; (△) Au particles prepared by the reduction of $HAuCl_4$ by sodium citrate, Au diameter = 20 nm; (□) ZnO powder prepared by neutralization of $Zn(NO_3)_2$ followed by calcination in air at 673 K.

and ZnO are not very different, 41.8 and 26.2 m^2/g respectively, and Cl^- contaminant always acts as a poison in CO oxidation, the fact that the temperature for 50% conversion of CO shifted, by adding gold to the zinc oxide, to lower temperature by more than 300 K indicates a significant combined effect of Au and ZnO.

Fig. 3a shows IR spectra obtained by introducing CO on an Au/ZnO sample, pretreated in pure oxygen up to 673 K and evacuated at RT. 80 mbar of CO (curve 1) produces a strong band at 2106 cm^{-1}, presenting an asymmetric broadening from the low frequency side. The band shape of this absorption can be well fitted by the superposition of two Lorentzian bands, one at 2106 cm^{-1}, FWHM = 9.6 cm^{-1}, and the other one at 2098 cm^{-1}, FWHM = 19.5 cm^{-1}. By reducing the equilibrium pressure the maximum of the absorption gradually blue-shifts up to 2118 cm^{-1} and the integrated intensity gradually decreases; however, the line broadening and the asymmetry from the low frequency side remain still present (fig. 3a, curves 2–6).

Fig. 3b shows the integrated intensities of the two bands obtained in the curve fits of the spectra shown in fig. 3a versus the wavenumber of the maxima. It appears evident that at low coverages (frequencies >2110 cm^{-1}) an almost linear relationship between the intensities and the maxima of the two bands is observed; at high coverages the low frequency band shows a lower intensity and the high frequency one a higher intensity than those extrapolated from the low coverage behaviour. The intensity transfer from the low to the high frequency band, evidenced by this analysis of the experimental data, is a clear indication that at high coverages a dynamic coupling occurs between the oscillators associated with the two bands. Also the vibrational bands of the adsorbed molecules shifting with the coverage, without significant changes in the shape of the bands, strongly indicate the occurrence of interadsorbate interactions. It is commonly found that the shift is the

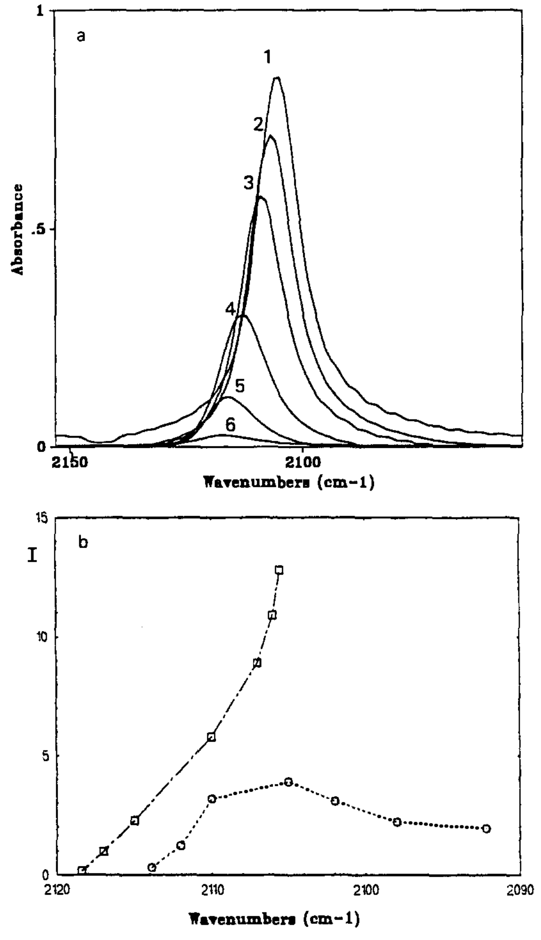


Fig. 3. (a) Au/ZnO Ir absorption spectra of CO adsorption in the carbonyl stretching region: curve 1, 50 mbar; curve 2, 15 mbar; curve 3, 1.5 mbar; curve 4, 0.2 mbar; curve 5, 0.02 mbar; curve 6, 0.002 mbar. (b) Integrated intensities of the two Lorentzian bands obtained in the curve fits of the spectra of (a) versus the frequencies of the maxima: (□) high frequency band; (○) low frequency band.

result of two components: a static or chemical effect and a dynamic or vibrational effect. The first one can produce shifts in both directions, the other one produces a shift always towards high wavenumbers [8].

Experiments with isotopic mixtures allow the separation of the two components. Fig. 4a shows the spectra produced by interaction between the sample and a 1 : 1 ^{12}CO–^{13}CO mixture at different equilibrium pressures. In the spectrum obtained by contacting the sample with 15 mbar of the mixture (fig. 4a, curve 1) a band at 2103 cm^{-1} and a band at 2056 cm^{-1} are observed. The two bands can be easily assigned to ^{12}CO and ^{13}CO molecules adsorbed on gold metallic sites; the two bands are significantly broader (apparent linewidth 22 cm^{-1}) than the band observed at 2106 cm^{-1} after interaction with pure ^{12}CO (linewidth $\approx$ 10 cm^{-1}).

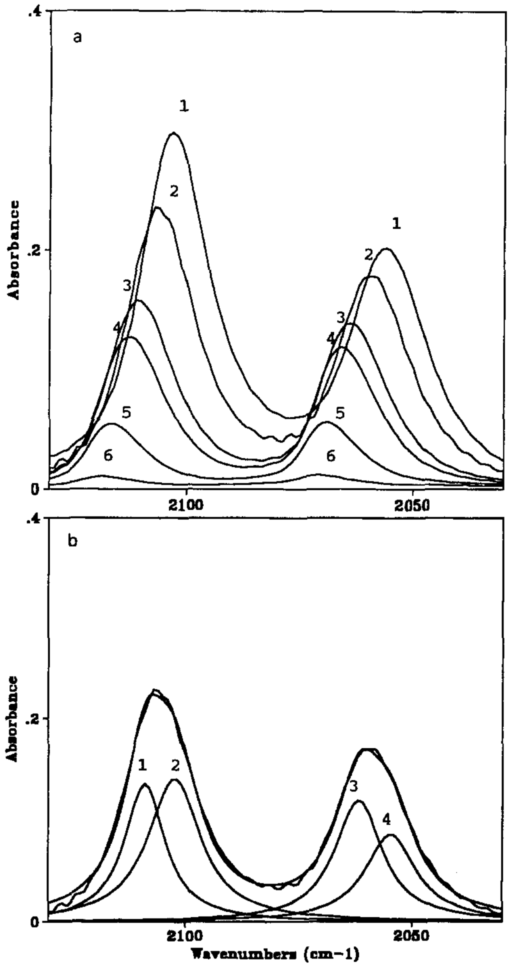


Fig. 4. (a) IR absorption spectra of the carbonyl stretching region produced by interaction of a 1 : 1 ^{12}CO–^{13}CO mixture: curve 1, 50 mbar; curve 2, 15 mbar; curve 3, 3 mbar; curve 4, 1.5 mbar; curve 5, 0.2 mbar; curve 6, 0.02 mbar. (b) Curve fit for curve 2 of (a).

The broadening is a consequence, as demonstrated by the curve fit shown in fig. 4b, of the fact that each absorption band, the 2103 and the 2056 cm^{-1} one, is made by the superposition of two bands, which are located very close to each other in frequency and exhibit a lower intensity difference than in pure ^{12}CO, at the same coverage. A good fit of curve 2 of fig. 4a is obtained by addition of four Lorentzian bands, one at 2109 cm^{-1}, FWHM = 11 cm^{-1}, integrated intensity (I) = 2.2 cm^{-1}, the second one at 2102 cm^{-1}, FWHM = 14 cm^{-1}, I = 2.8 cm^{-1}, the third at 2062 cm^{-1}, FWHM = 13 cm^{-1}, I = 2.2 cm^{-1} and the fourth at 2055 cm^{-1}, FWHM = 13.8 cm^{-1}, I = 1.7 cm^{-1}. The readmission of pure ^{12}CO after outgassing of the mixture produces an absorption spectrum with the same linewidth, shape and intensity as those shown in fig. 3a; therefore the differences in the linewidth between the mixture and the pure ^{12}CO can be explained by a lower degree of coupling between the oscillators in the mixture [5].

By reducing the equilibrium pressure the bands gradually reduce their intensities and shift towards high frequency up to 2118 and 2070 cm^{-1}, respectively. Moreover, it can be observed that at the maximum coverage (fig. 4a, curve 1) the two bands display a significant intensity difference, while at low coverages (fig. 4a, curves 5 and 6) the two bands have almost the same intensity. The change in the relative intensity of the two bands with the coverage is another clear indication that *the adsorption sites are mutually interacting and vibrationally coupled* [9], confirming the findings in the experiments with pure ^{12}CO. Another band is observed at 2002 cm^{-1} (not shown for the sake of brevity); the assignment of this last band, observed also in similar experiments on Au/TiO$_2$ [10] and on Au/SiO$_2$ [11], is not trivial and will not be discussed here.

In conclusion, the experiments illustrated in figs. 3 and 4 put in evidence that CO is adsorbed on two kinds of strongly interacting Au sites. Experiments, not shown for sake of brevity, of adsorption of 15 mbar of a 1 : 9 ^{12}CO–^{13}CO mixture showed that the ^{12}CO vibrationally decoupled by the other adsorbed molecules shows its maximum at 2095 cm^{-1}, 11 cm^{-1} lower than in pure ^{12}CO atmosphere at the same pressure. This shift is much smaller than the value of 53 cm^{-1} observed for Cu(111) surfaces [12]. A dipole–dipole coupling of 11 cm^{-1} on a Cu(111) plane corresponds to an estimated coverage of 0.13 monolayers [12], the equivalent of 0.17 monolayers on an Au(111) surface. As already stated, the isotopic mixture experiments were made at a pressure of 15 mbar; in view of the evidence coming from the intensity growth of the bands shown in fig. 3 that additional adsorption occurs above this pressure, taking the integrated intensity of the IR absorption band as a measure of the amount of the chemisorbed CO, a final coverage of 0.22 monolayers can be estimated. On Cu/ZnO samples [13] at full coverage at room temperature a surface coverage of the exposed copper sites with CO of 0.1 monolayers was experimentally determined by microgravimetric measurements; on the same sample the chemical shift put in evidence by ^{12}CO–^{13}CO mixture experiments, was similar to that expected for a 0.25 monolayer coverage [14]; to explain the discrepancy between the coverage determined by microgravimetric measurements and the coverage that can be deduced from the chemical shift data, it was hypothesized that CO molecules tend to aggregate on the more exposed, more protruding and more electropositivized step atoms. Probably, the same phenomenon occurs also on Au/ZnO samples, as testified by the quite large chemical shift observed.

The low frequency component, evidenced in the ^{12}CO spectrum, on the basis of the behaviour with the coverage, according to calculations of vibrational spectra of adsorbed islands of small dimensions [15] and according to our previous discussion of similar results on Au/TiO$_2$ [10] and on Cu/ZnO samples [13] can be assigned to the CO adsorption on metallic sites at the "perimeter" of the particle that is in contact with the metal oxide support. The higher intensity ratio of the high frequency band with respect to the low frequency one, observed at high coverages in the spectrum of pure ^{12}CO and the differences observed in the ^{12}CO–^{13}CO mixtures, leading to a change in the width of the band, can be interpreted as an indication that in the isotopic mixtures the coupling between the "internal" sites and the "perimeter" sites is reduced, leading to bands of more similar intensity.

Fig. 5a shows the spectrum obtained after admission on the sample of 0.5 mbar of ^{12}CO (curve 1), and the spectra recorded after inlet of $^{16}O_2$ (curve 2) and after inlet of $^{18}O_2$ (curve 3). It can be observed that, after few minutes of contact with $^{16}O_2$, the band initially observed at 2107 cm^{-1} reduces its intensity and shifts up to 2116 cm^{-1}, the low frequency broadening disappears and a new component at

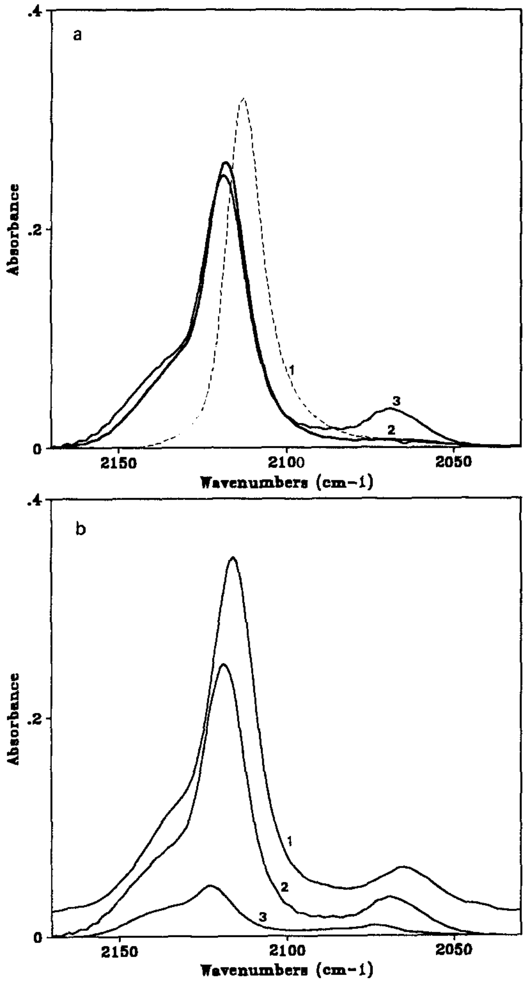


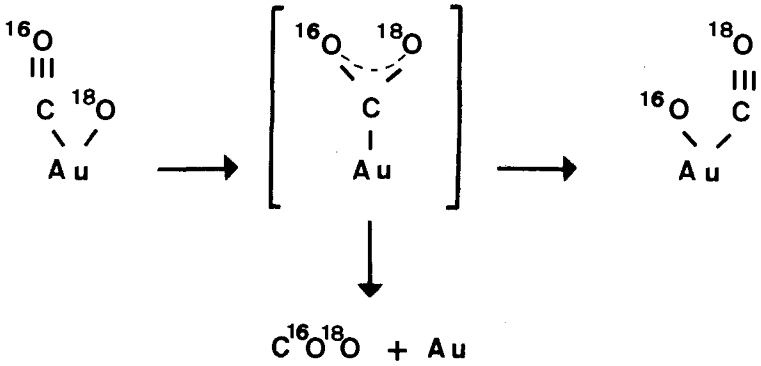
Fig. 5. (a) Comparison between the IR absorption spectra in the carbonyl stretching region produced by different interactions: curve 1, 0.5 mbar of CO; curve 2, inlet of 0.5 mbar of $^{16}O_2$; curve 3, inlet of 0.5 mbar of $^{18}O_2$. (b) IR absorption spectra of the carbonyl stretching region produced by interaction with a 1 : 1 CO–$^{18}O_2$ mixture: curve 1, 1 mbar; curve 2, 0.5 mbar; curve 3, 0.1 mbar.

2136 cm^{-1} appears (curve 2). At the same time, additional bands grow up in the 1700–1000 cm^{-1} range, typical of the carbonate-like species (not shown for simplicity) and molecular CO_2 is detected, in both IR and mass spectra. Similar results were observed some years ago on a Cu/ZnO sample [13]: after inlet of oxygen a band initially located at 2098 cm^{-1} was shifted up to 2116 cm^{-1} and a band initially observed at 2070 cm^{-1}, which was assigned to CO adsorbed on copper borderline atoms, was depleted and a new one was immediately observed at 2143 cm^{-1}.

IR studies of CO adsorbed on monocrystalline gold cannot be found in the literature up to now; however, studies on polycrystalline films [16] and oxide supported particles [17] confirm that the group IB metals exhibit a common behaviour. Hollins and Pritchard [18] showed that CO adsorption on oxidized Cu(110) surfaces produces a band at 2140 cm^{-1}, which was assigned to CO adsorbed on Cu atoms directly bonded to adsorbed oxygen. By analogy with the referred results the 2136 cm^{-1} band can be assigned to CO adsorbed on the oxidized gold sites at the perimeter; gold is far less oxidizable than copper, however, particularly highly uncoordinated and highly surface-exposed sites may show a special reactivity; the simultaneous disappearance of the low frequency component indirectly confirms that the sites involved are the most uncoordinated ones. Bands at 2130–2150 cm^{-1}, ascribed to CO adsorbed on "oxidized" gold sites were observed by SERS (surface enhanced Raman spectroscopy) after CO interaction on gold electrodes at positive potentials [19]. SERS active sites are usually considered to be highly uncoordinated, atypical sites; therefore, our assignment appears in agreement with the SERS observations.

In conclusion, it can be stressed that the above illustrated experiment put in evidence that on Au/ZnO samples there are highly uncoordinated gold sites able to chemisorb both oxygen and carbon monoxide. When the same experiment is performed with $^{18}O_2$ instead of $^{16}O_2$ (fig. 5a, curve 3), in addition to the previously illustrated features, a new, well defined band at 2068 cm^{-1} immediately appears. Also, this band, as the other ones in the same spectral region, shifts towards high frequencies by reducing the pressure (fig. 5b, curves 2 and 3) and is completely depleted by outgassing. On the basis of this behaviour and of its frequency the band can be assigned to $C^{18}O$ molecules adsorbed on gold surface sites. This assignment is also supported by quadrupole mass analysis experiments of the gas phase, in which peaks at $m/z = 30$, 46 and 48 were detected, that can be ascribed to $C^{18}O$, $C^{16}O^{18}O$ and $C^{18}O_2$ species.

Given the weak nature of the bonding between gold and carbon monoxide, it seems unlikely that the oxygen exchange reaction in carbon monoxide molecules occurs through a mechanism of dissociation and recombination. Therefore, a concerted exchange mechanism between the two adsorbed species, carbon monoxide and oxygen, is proposed. The adsorption on the same gold site of carbon monoxide and of oxygen, evidenced by the band at 2138 cm^{-1}, can be a favorable intermediate for the exchange and for the oxidation reaction of the CO in mild conditions (see scheme 1).



Scheme 1.

4. Conclusion

The experimental data here presented evidence that:

(i) Au/ZnO catalysts prepared by coprecipitation expose gold sites which are able to adsorb both oxygen atoms and carbon monoxide at the same time;

(ii) the samples produce at *room temperature* a scrambling reaction between $C^{16}O$ and ^{18}CO, leading to the formation of $C^{18}O$.

References

[1] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet and B. Delmon, J. Catal. 144 (1993) 175, and references therein.
[2] J. Saussey, J.C. Lavalley and C. Bovet, J. Chem. Soc. Faraday Trans. I 78 (1982) 1457.
[3] F. Boccuzzi, G. Ghiotti and A. Chiorino, Surf. Sci. 162 (1985) 361.
[4] G. Ghiotti, F. Boccuzzi and A. Chiorino, in: *Adsorption and Catalysis on Oxide Surfaces*, eds. M. Che and G.C. Bond (Elsevier, Amsterdam, 1985) p. 235.
[5] F. Boccuzzi, A. Chiorino, S. Tsubota and M. Haruta, in preparation.
[6] G. Carnisio, F. Garbassi, G. Petrini and G. Parravano, J. Catal. 54 (1978) 66.
[7] S.D. Jackson, J. Catal. 108 (1987) 250.
[8] M.W. Roberts, Chem. Soc. Rev. 18 (1989) 451, and references therein.
[9] P. Hollins, Surf. Sci. Rep. 16 (1992) 53.
[10] F. Boccuzzi, S. Tsubota and M. Haruta, J. Electron Spectry. Rel. Phenom. 64/65 (1993) 241.
[11] J. France and P. Hollins, J. Electron Spectry. Rel. Phenom. 64/65 (1993) 251.
[12] P. Hollins and J. Pritchard, Surf. Sci. 89 (1979) 456.
[13] F. Boccuzzi, G. Ghiotti and A. Chiorino, Surf. Sci. 156 (1985) 933.
[14] G. Ghiotti, F. Boccuzzi and A. Chiorino, Surf. Sci. 178 (1986) 553.
[15] S.F. Ippolitova, I.V. Kumpanenko and R.S. Sorbello, Surf. Sci. 118 (1982) 415.
[16] P. Dumas, R.G. Tobin and P.L. Richards, Surf. Sci. 171 (1986) 555.
[17] A. Knell, P. Barnickel, A. Baiker and A. Wokaun, J. Catal. 137 (1992) 306.
[18] P. Hollins and J. Pritchard, Surf. Sci. 123 (1982) 38.
[19] M.A. Tadayyoni and M.J. Weaver, Langmuir 2 (1986) 179.