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# Comparative IR diffuse reflectance study of fundamental C=O stretching and combination C=O plus M–C stretching vibrational modes of CO linearly adsorbed on $Ir/Al_2O_3$ catalyst

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Using diffuse reflectance IR spectroscopy, the comparative analysis of absorption bands corresponding to fundamental C=O stretching and combination C=O plus M–C stretching vibrational modes for $^{12}CO$ and $^{12}CO + {}^{13}CO$ mixtures adsorbed on metallic Ir in supported 6% $Ir/Al_2O_3$ catalyst was performed. For CO adsorbed on metal in linear form the frequencies and intensities of combination absorption bands were insensitive to dipole–dipole coupling between adsorbed molecules. Therefore the carbon–metal bond stretching frequency could be calculated as the frequency difference of the combination mode and the singleton. For the linear form of carbon monoxide adsorption on supported Ir it is equal to 475 $cm^{-1}$.

**Keywords:** DR-IR spectroscopy; supported Ir; adsorption of CO; combination modes

## 1. Introduction

The linear form of carbon monoxide adsorption with IR control of CO bond fundamental stretching frequency is widely used as a spectroscopic probe in the study of supported metals. Even though this bond is not directly involved in the interaction with the metal surface, it provides important information on the electronic properties of small metal particles as well as on "ensemble size" and "ligand" effects resulting from formation of alloys [1,2].

Unfortunately, for inhomogeneous systems represented by supported metals this approach is restricted by strong lateral interaction between adsorbed CO molecules resulting in dipole–dipole shifts [3,4] and in effective redistribution of the intensities between low frequency and high frequency absorption bands [5,6]. Therefore the different adsorption sites of metallic particles can be hardly distinguished from such experiments.

Another interesting alternative is the characterization of metal surfaces by the

frequency of metal–carbon vibrations ($\nu_{M-C}$) of adsorbed CO which have been directly determined for CO adsorbed on bulk metals by modern spectroscopic techniques [7,8]. There is no doubt that this frequency is more directly connected with the adsorption bond. In addition it is more sensitive to the nature of different metals changing from 350 $cm^{-1}$ for Cu to 480 $cm^{-1}$ for Pt [8]. The M–C stretching frequency is much less sensitive to dipole–dipole coupling between adsorbed molecules than that of C=O bond [9]. There is also a linear relationship between $\nu^2_{M-C}$ and CO adsorption heats [8]. Unfortunately, for supported metals the direct observation of M–C vibrations is practically impossible due to the strong light absorption created by metal–oxygen bond vibrations of the oxide carriers in the 300–500 $cm^{-1}$ spectral range. Nevertheless, this frequency can be obtained with the accuracy of several wave numbers indirectly as the difference of $\nu_{C=O} + \nu_{M-C}$ combination mode and C=O fundamental stretching vibration. Although the intensities of the combination adsorption bands are more than two orders of magnitude lower than those of C=O stretching vibrations for some supported metals with loadings of several percents ($Pt/TiO_2$, $Pt/Al_2O_3$) these bands have been clearly detected either by transmittance [10] or by diffuse reflectance IR spectroscopy [11].

The aim of this report is the comparative IR study of CO adsorption on aluminum supported iridium in fundamental $\nu_{C=O}$ and combination $\nu_{C=O} + \nu_{M-C}$ regions.

## 2. Experimental

Aluminum oxide supported iridium catalyst with metal loading of 6 wt% was prepared by impregnation of $\gamma$-$Al_2O_3$ (A-64 grade, BET surface area of 180 $m^2/g$) with aqueous solution of $H_3IrCl_6$. After reduction in flowing $H_2$ at 570 K the sample was passivated at room temperature in helium flow containing 0.2 vol% of oxygen. Before spectral measurements the catalyst was additionally reduced with hydrogen under static conditions ($P = 100$ Torr) at 770 K for 2 h followed by evacuation at the same temperature for 1 h. The "dispersion" of metallic iridium was determined by means of $H_2$ or CO chemisorption at 300 K. It was equal to $H/Ir = 0.65$ or $CO/Ir = 0.33$.

IR diffuse reflectance spectra of adsorbed CO were measured at room temperature in the ranges of 1700–2300 and 2400–2650 $cm^{-1}$ with a double beam Perkin-Elmer 580 B spectrophotometer as described in ref. [12]. Saturation of metallic iridium surface with adsorbed CO was performed at room temperature and equilibrium CO pressure of 10 Torr. The gradual decrease of metal surface coverage was achieved by successive sample evacuation at 300, 370, 470, 570, 620, 670 and 720 K for 1 h at each temperature.

Before use hydrogen and carbon monoxide were purified from traces of oxygen and water by successive passing through the columns filled with 4A molecular sieve and reduced chromium–silica catalyst.

## 3. Results and discussion

Fig. 1 represents the evolution of CO fundamental stretching vibrational spectra recorded after carbon monoxide adsorption at 300 K on 6% $Ir/Al_2O_3$ and successive sample evacuation at elevated temperatures. In the presence of gaseous CO three bands are observable. They correspond to bridged (1845 $cm^{-1}$) and linear (2085 $cm^{-1}$) forms of CO adsorption on metal particles [13,14] and to CO complexes with coordinatively unsaturated $Al^{3+}$ cations of the support (2210 $cm^{-1}$) [15]. The bridging species as well as those adsorbed on $Al^{3+}$ cations are thermally unstable and can be completely removed by sample evacuation at 370 K.

After sample evacuation at 470 K the band of linear CO complexes is shifted towards lower frequency of 2060 $cm^{-2}$, the resolution of the shoulder at 2020 $cm^{-1}$ is improved and a new band with the maximum at 2095 $cm^{-1}$ becomes evident. The latter two bands are similar to those earlier observed for $Ir_4(CO)_{12}$ or $Ir(CO)_3Cl$ carbonyls [13,16] and therefore should be ascribed to surface iridium polycarbonyls. They are stable up to 620 K, while above this temperature the only remaining band is the one of the linearly adsorbed carbon monoxide with the maximum at 2008 $cm^{-1}$. It is stable in vacuum even at 720 K. Thus, this band from the most thermally stable linearly adsorbed CO molecules exhibits in the course of metal surface coverage decrease of the low frequency shift by 75 $cm^{-1}$ from 2085 $cm^{-1}$ for the surface saturated with adsorbed molecules to the singleton frequency of 2008 $cm^{-1}$. This is connected with the weakening of the dipole–dipole coupling between adsorbed molecules at lower surface coverages.

The combination $\nu_{C=O} + \nu_{M-C}$ absorption bands of the linear form of adsorbed CO at saturation metal surface coverage (a) and after sample evacuation at 670 K (b) are represented in fig. 2. In both cases signal to noise ratio exceeds 5 and the

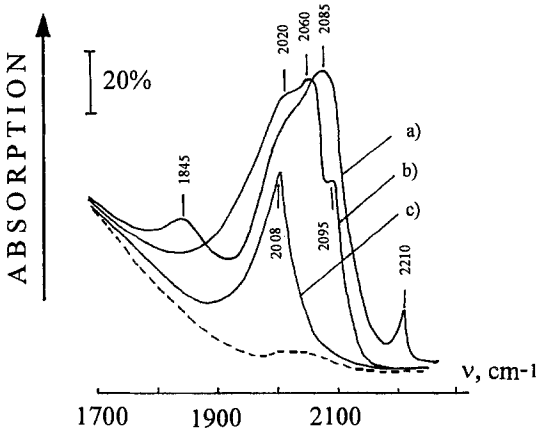


Fig. 1. IR spectra of CO adsorbed on 6% $Ir/Al_2O_3$ in the presence of 10 Torr of gaseous CO (a) and after sample evacuation at 470 K (b) and 720 K (c). The background is shown by the dashed line. Spectra were measured at room temperature.

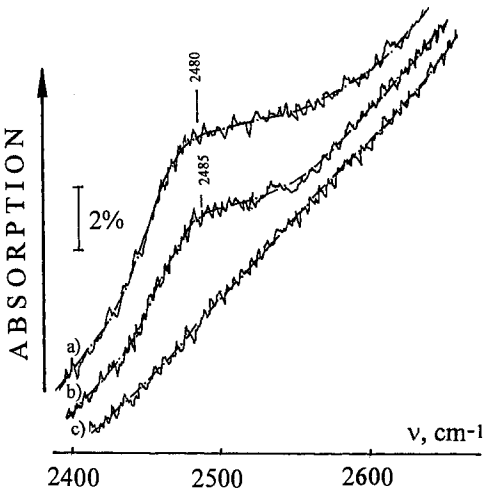


Fig. 2. IR spectra of combination $\nu_{C=O} + \nu_{M-C}$ modes for linearly adsorbed CO on metallic Ir at saturation metal surface coverage (a) and after sample evacuation at 670 K (b) and 770 K (c). Spectra were measured at room temperature.

positions of the maxima in averaged spectra obtained after background subtraction coincide within an accuracy of 5 $cm^{-1}$.

On the other hand, the corresponding stretching C=O frequencies of these samples differ for 55 $cm^{-1}$ (fig. 1 (a) and (c)). This means that unlike the C=O stretching mode the combination $\nu_{C=O} + \nu_{M-C}$ vibration is not influenced by the dipole–dipole coupling. Therefore the latter is more characteristic than the stretching mode and can be well approximated as the sum of singleton and metal–carbon frequencies. This is confirmed by theoretical analysis and the experimental data earlier obtained for unsupported metallic Pt [7]. A similar phenomenon was also observed by us in ref. [11] for linear CO complexes on aluminum oxide supported platinum catalysts.

The dipole–dipole interaction does not also average the combination absorption bands of adsorbed molecules with different frequencies. This follows from the experiments with $^{13}CO + {}^{12}CO$ mixtures of different composition at saturation metal coverage (adsorption at room temperature and CO pressure of 10 Torr) (fig. 3). For 90% $^{13}CO$ + 10% $^{12}CO$ mixture (fig. 3 (c)) the shape and intensity of the adsorption band are similar to those for pure $^{12}CO$ (fig. 3 (a)), but the position of the maximum is shifted by 55 $cm^{-1}$ towards the lower frequencies. This frequency difference almost coincides with that of $^{12}CO$ and $^{13}CO$ stretching vibrations. Hence the 2425 $cm^{-1}$ absorption band is related with a combination mode of linear complexes of almost pure $^{13}CO$ molecules.

The adsorption of 30% $^{13}CO$ + 70% $^{12}CO$ mixture results in two poorly resolved bands at 2425 and 2480 $cm^{-1}$ corresponding to combination modes of linear complexes of metallic Pt with $^{13}CO$ and $^{12}CO$ respectively (fig. 3 (b)). The ratio of their integrated intensities is about 1 : 2. This is close to isotope composition of the

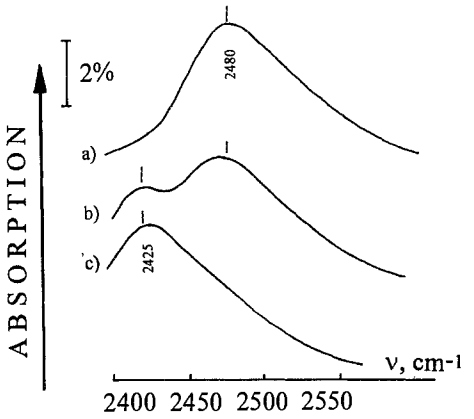


Fig. 3. IR spectra of combination $\nu_{C=O} + \nu_{M-C}$ modes for $^{12}CO$ (a) and for mixtures 30% $^{13}CO$ + 70% $^{12}CO$ (b) and 90% $^{13}CO$ + 10% $^{12}CO$ (c) adsorbed on metallic Ir at saturation metal surface coverage. Spectra were measured at room temperature.

adsorbate and indicates the absence of the intensity redistribution effect between low-frequency and high-frequency absorption bands that is characteristic of fundamental stretching vibrations [5,6].

These results show that lateral interactions between CO molecules adsorbed on supported metals do not influence the IR combination modes of the linear complexes. Therefore the combination bands can be used for detailed study of the heterogeneity of adsorption sites at arbitrary metal surface coverages with adsorbed CO. This conclusion is also supported by the following results.

Fig. 4 represents the IR spectra of carbon monoxide preadsorbed at 300 K and evacuated at 670 K before and after additional saturation of supported iridium cat-

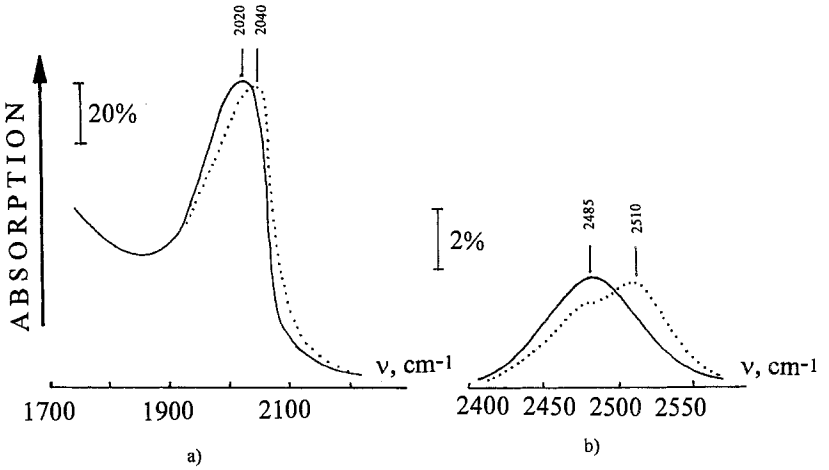


Fig. 4. IR spectra of CO chemisorbed in linear form on metallic Ir before (——) and after (. . .) saturation of supported iridium catalyst with hydrogen at 300 K: (a) fundamental stretching vibrations of C=O bond; (b) combination $\nu_{C=O} + \nu_{M-C}$ modes. Spectra were measured at room temperature.

alyst with hydrogen at 300 K. It is evident that after hydrogen chemisorption the maximum of the fundamental stretching CO band at 2020 $cm^{-1}$ is shifted by 20 $cm^{-1}$ toward higher frequencies without any evidence of appearance of new bands (fig. 4a). On the contrary, the spectrum of the corresponding combination mode is split after hydrogen chemisorption into two poorly resolved components with maxima at 2475 and 2510 $cm^{-1}$ (fig. 4b). This indicates the appearance after hydrogen chemisorption of at least two types of linear surface CO complexes that cannot be distinguished in the CO fundamental stretching region.

## 4. Conclusion

Our results show that a detailed and systematic study of combination modes of adsorbed CO molecules could initiate a new approach in the spectroscopic study of supported metal catalysts. Indeed, the combination C=O plus metal–carbon stretching vibrations of carbon monoxide adsorbed in linear form on 6% $Ir/Al_2O_3$ catalyst are more characteristic than the fundamental C=O stretching vibrations. The positions of such combination bands are independent of the metal surface coverage and therefore are insensitive to the dipole–dipole coupling between adsorbed CO molecules. This is also consistent with the absence of the averaging of combination bands of isotope labeled molecules that is characteristic of the fundamental CO stretching bands. Therefore the carbon–metal stretching frequency can be calculated as the difference of the combination mode and C=O stretching frequencies.

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