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# Spectroscopic Evidence for Rh–CO–$Zr^{4+}$ Surface Species Formed on $Rh/ZrO_2$ Catalyst

$Rh/ZrO_2$ prepared from Rh carbonyls contains highly dispersed Rh crystallites and is interesting as a catalyst for syngas conversion to $C_2$-oxygenated molecules (*1, 2*). In particular, the selectivity to ethanol seems to be increased for Rh supported or promoted by metal oxides showing both acid and basic properties, such as $TiO_2$ (*1*), $ZrO_2$ (*1, 2*), and $V_2O_3$ (*3*). Notwithstanding the different and partially conflicting hypotheses (*1–3*) on the mechanism of formation of ethanol and other oxygenated molecules, there is no doubt that the promoter effect of the support influences the temperature of CO dissociation (*1*): this temperature is lowered from 483 K for $Rh/SiO_2$ to 448 K for $Zr^{4+}$-promoted Rh–Zr (1 : 1)/$SiO_2$ catalyst. Similar results are obtained for $Rh/SiO_2$ promoted by oxidic phases of Ti, V, and Mn located at the surface of Rh particles (*1*).

Evidence for this effect is given by the IR spectra of CO adsorbed on these systems at room temperature (RT) after reduction at 673 K. These spectra show the usual linear and bridged CO species on $Rh^0$ at 2040–2060 and 1880 $cm^{-1}$, respectively, accompanied by a broad and not well resolved shoulder between 1750 and 1520 $cm^{-1}$ (1670 $cm^{-1}$ for the Zr-promoted catalyst). These low-frequency CO bands have been assigned, in accord with the spectral position of analogous homogeneous species (*4*), to a tilted CO group, C-bonded to $Rh^0$ and O-bonded to the promoter metal ion. The formation of this surface species evidently favors the CO dissociation process.

To ascertain if a similar species is formed on a $Rh/ZrO_2$ system, the author has carried out an accurate Fourier transform–infrared (FT-IR) spectroscopic investigation. No such study has yet been reported, although in one paper presented at a recent conference (*5*) the same system and a FT-IR photoacoustic spectroscopic technique were utilized. However, the photoacoustic spectra (PAS) are not of particularly high resolution and oxidation of CO with formation of $CO_2$, carbonates, and $Rh^{+1}$–CO species is evident.

$ZrO_2$ with a BET surface area of 80 $m^2/g$ was prepared by hydrolysis of $ZrO_2$ with aqueous ammonia followed by drying at 383 K and calcination at 823 K. This oxide, containing monoclinic and tetragonal crystals in a 50 : 50 ratio, was impregnated with a pentane solution of $Rh_4(CO)_{12}$, (1% Rh), and the solvent was then evaporated. After treatment at 573 K in $H_2$ all carbonyl groups were eliminated (as shown by the IR spectrum) and a survey experiment of CO adsorption was then performed at room temperature (RT). The spectra have been recorded with a Perkin–Elmer FT-IR 1760 instrument with 4-$cm^{-1}$ resolution and number of scans $\geq$ 200.

The sample was reduced in the IR cell at 773 K with a final outgassing of 20 min at this temperature. Subsequent examination by TEM showed very small Rh particles ($\bar{d}$ = 14 Å) to be present. The sample was brown and had a low transparency in the IR range 3000–1000 $cm^{-1}$ ($T\%$ max = 0.14 at 1700 $cm^{-1}$). Some residual carbonate groups appeared in the background between 1600 and 1300 $cm^{-1}$, further lowering the low transparency in this range.

In Fig. 1 are shown the spectra obtained after increasing doses of CO had been adsorbed at RT on the 773 K reduced sample

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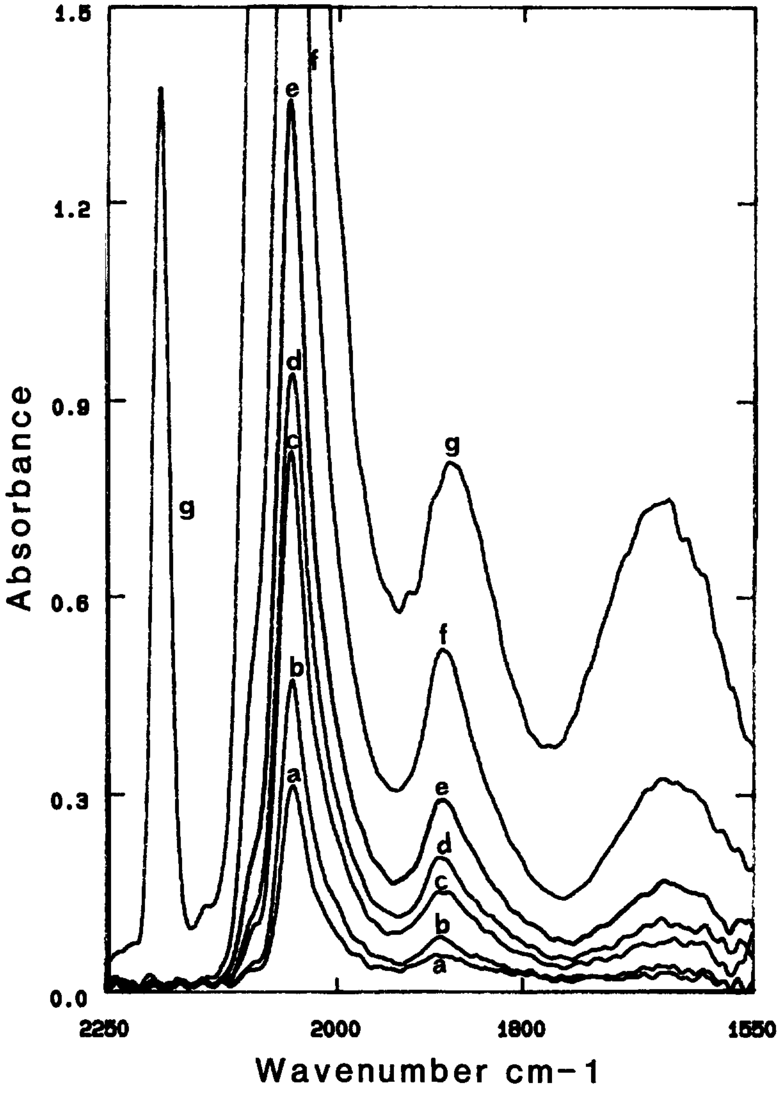


FIG. 1. IR spectra at room temperature (RT) after CO adsorption at increasing coverages on $Rh_4(CO)_{12}/ZrO_2$ catalyst which had been reduced for 2 h and outgassed for 20 min at 773 K. The final pressures (in Torr) of CO after adsorption are (a–e) $p = 0$, (f) $p = 1 \times 10^{-1}$, and (g) $p = 30$.

up to saturation, namely curve g at $p = 30$ Torr (1 Torr = 133.3 N $m^{-2}$). The spectra clearly show the formation of four CO adsorbed species, which can be summarized as follows:

1. A species absorbing at 2191 $cm^{-1}$ which occurs only under a finite CO pressure. This is assigned to CO weakly chemisorbed on $ZrO_2$, i.e., to a $Zr^{4+}$–CO complex, in accord with literature data (*6*, *7*).
2. A species associated with a band at 2048 $cm^{-1}$.
3. A species growing in parallel with a band at 1890–1880 $cm^{-1}$. This band and that at 2048 $cm^{-1}$ can be assigned to CO adsorbed on $Rh^0$ in bridged form and linear form, respectively. Two weak shoulders at 2092 and 2020 $cm^{-1}$ in the low- and high-frequency tails of the 2048 $cm^{-1}$ band can be assigned to small amounts of geminal $Rh^{+1}(CO)_2$ complexes (*8*).

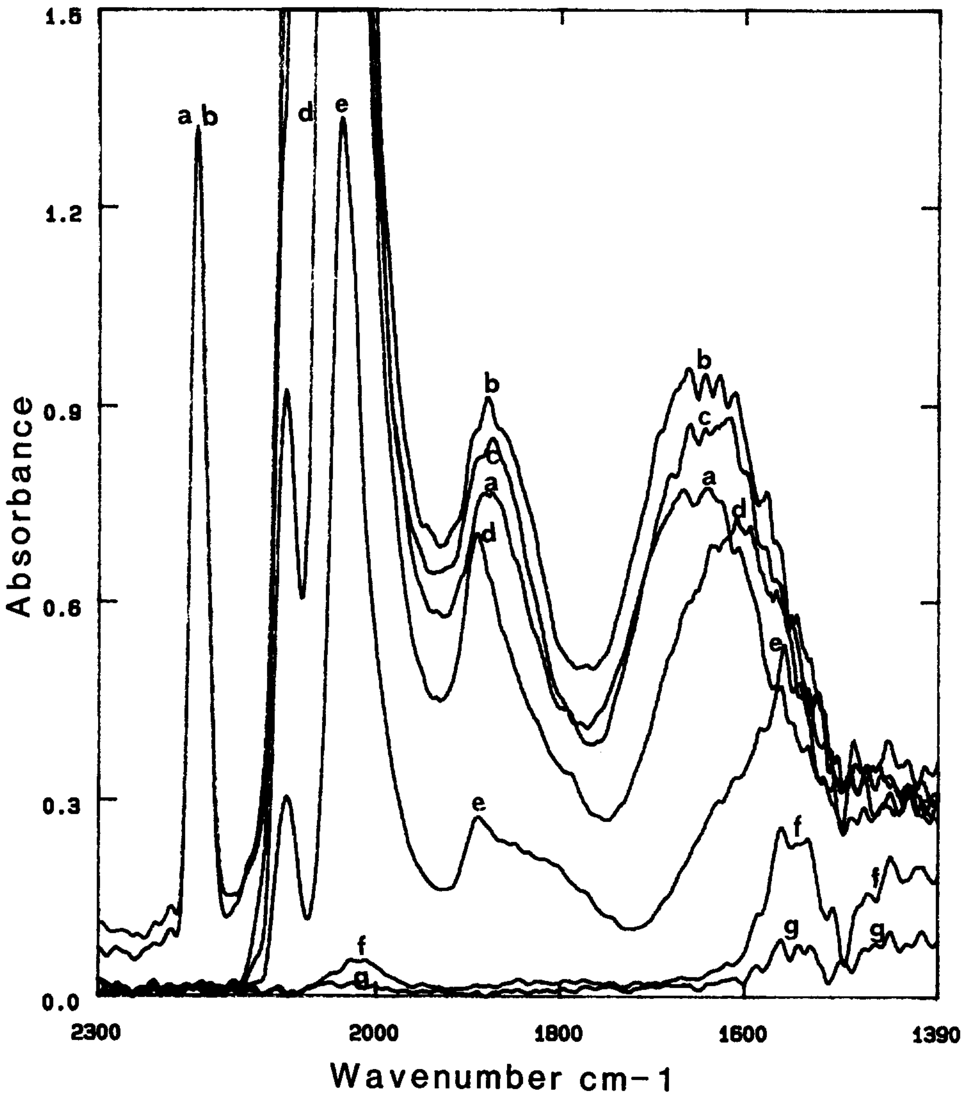


FIG. 2. IR spectra after CO desorption from the sample shown in Fig. 1 at increasing temperature. (a) $p_{CO}$ = 30 Torr, spectrum recorded immediately and (b) after 16 h; (c) after 1 min evacuation at RT; (d–g) RT spectra after CO had been desorbed for 20 min at 373, 473, 573, and 623 K, respectively.

4. A species which gives a broad band at 1660 $cm^{-1}$, reaching at maximum coverage the same intensity as the bridged species (curve g).

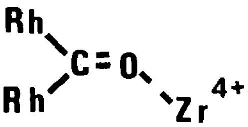
However, the formation of a 1660 $cm^{-1}$ band with minor intensity also occurred for CO adsorbed in a survey experiment on a sample reduced at 573 K and is immediate after adsorption of large doses of CO. *Because no other bands due to linear* $CO_2$ *or carbonate species are observed in all these experiments, the CO oxidation process is excluded at RT and the 1660* $cm^{-1}$ *band cannot be assigned to carbonate groups.*

Experiments on CO desorption at increasing temperatures demonstrate a lack of full reversibility. Data for the sample of Fig. 1 are shown in Fig. 2. After 16 h in CO an increase in a component at 1620 $cm^{-1}$ is observed (curve b). This is assigned to the bending mode of water molecules which have slowly desorbed from the walls of the quartz cell and have transferred to the hydrophilic support. At RT the 2191 $cm^{-1}$ band is completely eliminated by evacuation.

At 373 K (curve d) the band assigned to linear CO decreases together with the low-frequency component at 1870 $cm^{-1}$ of the bridged species. Between 373 and 473 K a strong decrease is also observed for the 1660 $cm^{-1}$ band, leaving residual bands at $\approx$1550 $cm^{-1}$ and 1420 $cm^{-1}$, assigned to carbonates. Therefore, under these conditions, the formation of carbonates and of $Rh^{+1}(CO)_2$ complexes at 2095 and 2020 $cm^{-1}$ is clearly shown to occur at the same time.

Between 373 and 473 K the CO adsorbed species partially dissociate and this finding coincides with the temperature of 448 K found by Ichikawa *et al.* (*1*) for the dissociation of CO adsorbed on $Zr^{4+}$-promoted Rh catalyst and with the temperature of $CO_2$ evolution found by TPD experiments on the same $Rh/ZrO_2$ system (*5*). Finally, after desorption at 573–623 K all types of adsorbed CO are completely removed.

Note that the frequency of linearly adsorbed CO is lowered, during the desorption experiments, from 2050 $cm^{-1}$ at RT to 2038 $cm^{-1}$ at 473 K and to 2020 $cm^{-1}$ at 573 K; also, part of the bridged CO shows a similar shift to lower wavenumber (see the shoulder at $\approx$1820 $cm^{-1}$ in Fig. 2, curve e). This shift to lower wavenumber of $\nu_{(CO)}$ is well known to occur for CO adsorbed on supported metals (*9*) and can be attributed to an annealing of the strongly adsorbed CO layer at $T >$ RT with a reduced crowding of adsorbed molecules: as a consequence a minor contribution of dipole–dipole and lateral effects on the high-frequency shift is expected. On a 573 K reduced sample the frequency of the first dose of linear CO is 2025 $cm^{-1}$, shifting to 2035 $cm^{-1}$ at high coverage: in this case the observation of a frequency lower than that of CO on the 773 K reduced sample can be explained as due to the smaller size of 573 K reduced Rh crystals with a consequent minor dipole–dipole effect (*9*).



SCHEME 1

As far as the band at 1660 $cm^{-1}$ is concerned, its spectral position and its thermal behavior can be well explained on the basis of a bridged CO species bonded at the borderline of $Rh^0$ particles through the C atom but also bridge-bonded to the coordinatively unsaturated $Zr^{4+}$ ions through the O atom as shown in Scheme 1. Under strongly reducing conditions at 773 K the formation of $Zr^{3+}$ ions cannot be excluded [see the weak CO band at 2132 $cm^{-1}$ (*7*)].

According to the hypothesis of Ichikawa and Sachtler (*1, 10*), there is a clear evidence here of the formation of a Shriver-type CO dative complex (*4*), precursor of an easier CO dissociation.

In agreement with the data reported here, some preliminary results with an $H_2/CO$ mixture confirm that between 423 and 473 K, the CO species at 1660 $cm^{-1}$ fully reacts and disappears with formation of bands due to ethoxy species (at 1142 $cm^{-1}$) and both $CH_3$ and $CH_2$ groups between 2980 and 2850 $cm^{-1}$ (*7*).

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