

Research Note

# New type of rhodium gem-dicarbonyls formed in Rh-ZSM-5: An FTIR spectroscopy study

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## Abstract

CO adsorption on Rh-ZSM-5 leads to the formation of both the well-known  $\text{Rh}^+(\text{CO})_2$  gem-dicarbonyls and another kind of dicarbonyl species as yet unknown. The latter are most probably formed with the participation of  $\text{Rh}^{n+}$  ( $n > 1$ ) ions in cationic positions in the zeolite. These species are characterized by  $\nu_s(\text{CO})$  at  $2176\text{ cm}^{-1}$  and  $\nu_{\text{as}}(\text{CO})$  at  $2142\text{ cm}^{-1}$ . The dicarbonyl structure is proven by  $^{12}\text{CO}$ – $^{13}\text{CO}$  coadsorption. In excellent agreement with the theoretically expected values, the mixed complexes,  $\text{Rh}^{n+}(\text{CO})_2$ , were characterized by  $\nu(^{12}\text{CO})$  at  $2164\text{ cm}^{-1}$  and  $\nu(^{13}\text{CO})$  at  $2106\text{ cm}^{-1}$ . In contrast to the classical gem-dicarbonyls, the new species are destroyed in the presence of water. This is consistent with the proposed higher oxidation state of rhodium in this case.

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## 1. Introduction

The carbonyl complexes of supported rhodium have been a subject of steady interest [1–26]. It is well established that CO adsorption of rhodium-containing catalysts results in the formation of  $\text{Rh}^+(\text{CO})_2$  species characterized by  $\nu_s(\text{CO})$  at 2120–2075 and  $\nu_{\text{as}}(\text{CO})$  at 2053–1990  $\text{cm}^{-1}$  [1–25]. Most of the investigations of CO adsorption on supported rhodium catalysts have been performed with prerduced samples. Because of the high stability of the gem-dicarbonyls of  $\text{Rh}^+$ , they are produced via oxidation of metallic rhodium, and most authors believe that the support surface hydroxyl groups are involved in the process [20–25]. There have been few studies of nonreduced rhodium-containing samples [21,26]. Several authors have reported carbonyl bands at relatively higher frequencies and assigned them to  $\text{Rh}^{n+}$ –CO species ( $n > 1$ ) [7–9,19,20,26]. In this paper we report the formation of new types of rhodium dicarbonyl com-

plexes formed with rhodium cations in an oxidation state higher than 1+. These species are produced in an Rh-ZSM-5 sample, and presumably the high coordinative unsaturation of cations in zeolites contributes to their formation. Indeed, some authors have reported [26] that  $\text{Rh}^+$  cations in Rh-ZSM-5 are low coordinated and can accommodate up to four CO molecules. In this paper we report on the formation of the as-yet unknown rhodium dicarbonyl species.

The starting H-ZSM-5 material, supplied by Degussa, had a Si/Al ratio of 26.8. Rh-ZSM-5 was prepared by solid-state ion exchange; 1.5 g of H-ZSM-5 was mixed with 0.15 g  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ , the mixture was ground in an agate mortar, and then placed in a quartz reactor and heated to 773 K in a nitrogen flow for 1 h. The nominal rhodium concentration in the sample was 3.7 wt% Rh and corresponded to an exchange degree of ca. 60%.

The IR spectra were recorded on a Nicolet Avatar 360 spectrometer at a spectral resolution of  $2\text{ cm}^{-1}$  and accumulation of 128 scans. A self-supporting pellet (ca.  $15\text{ mg cm}^{-2}$ ) was prepared from the sample powder and treated directly in a purpose-made IR cell. The latter was connected to a vacuum-adsorption

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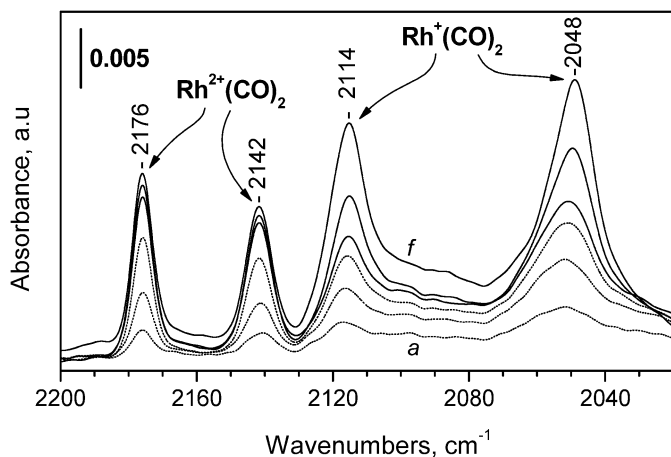


Fig. 1. FTIR spectra taken after introduction of small doses of CO (1 dose = 0.11  $\mu\text{mol}$ ) to reduced Rh-ZSM-5: 2, 3, 4, 5, 16 and 70 doses (a–f).

apparatus with a residual pressure  $<10^{-3}$  Pa. Carbon monoxide ( $>99.997$ ) and nitrogen monoxide ( $>99.9$ ) were supplied by Air Liquide, France. Labeled carbon monoxide ( $^{13}\text{C}$  isotopic purity of 92.9 at%) was delivered from CEA-ORES, France. Before use, carbon monoxide and oxygen were passed through a liquid nitrogen trap.

Before the adsorption measurements, the sample was activated by 24-h evacuation at ambient temperature, followed by 1 h of heating at 673 K in oxygen, evacuation for 1 h at the same temperature, and reduction in CO (13.3 kPa) at 523 K. Then CO was evacuated initially at ambient temperature and then at 523 K. No carbonyl bands were detected in the IR spectrum after this treatment.

Adsorption of CO at ambient temperature on the sample was initially performed with small doses added successively into the cell. The first dose of adsorbed CO provoked the appearance of four bands with maxima at 2176, 2142, 2114, and 2048  $\text{cm}^{-1}$  (Fig. 1, spectrum a). All bands increased in intensity with the amount of CO introduced into the IR cell (Fig. 1, spectra b–d). Analysis of the spectra shows two sets of bands changing in parallel, at 2176 and 2142  $\text{cm}^{-1}$  on the one hand, and at 2114 and 2048  $\text{cm}^{-1}$  on the other hand. The bands at 2114 and 2048  $\text{cm}^{-1}$  went on increasing after the bands at 2176 and 2142  $\text{cm}^{-1}$  reached saturation. Under increasing CO equilibrium pressure, new bands at 2195, 2118 and 2084  $\text{cm}^{-1}$  appeared, whereas the bands at 2114 and 2048  $\text{cm}^{-1}$  decreased in intensity (Fig. 2, spectra a–c). No changes in the O–H stretching region were detected, indicating that the OH groups were not involved in the formation of the carbonyl species. This situation differs from the case where CO is adsorbed on samples containing metallic rhodium and where oxidation of metallic rhodium by the surface support hydroxyls is well established [16].

The bands at 2114 and 2048  $\text{cm}^{-1}$  are unambiguously assigned to the  $\nu_{\text{s}}(\text{CO})$  and  $\nu_{\text{as}}(\text{CO})$  modes, respectively, of the well-known  $\text{Rh}^+(\text{CO})_2$  gem-dicarbonyls [1–25]. The bands at 2118 and 2084  $\text{cm}^{-1}$  characterize tricarbonyls produced by insertion of a third CO molecule into the  $\text{Rh}^+(\text{CO})_2$  species [21,26]. The band at 2195  $\text{cm}^{-1}$  is seen at high equilibrium pressure only (Fig. 2, spectra a and b) and is due to carbonyls of

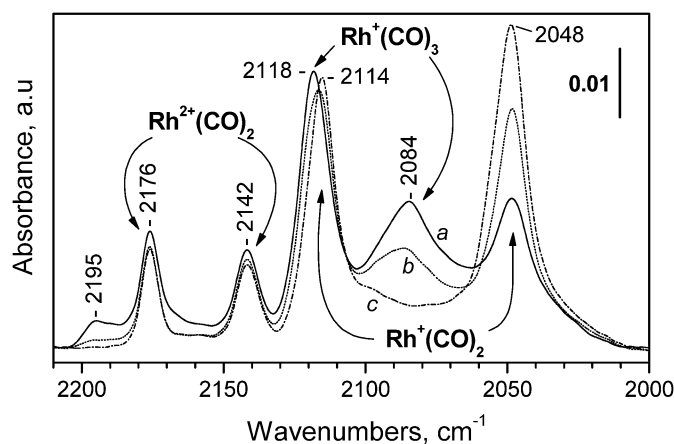


Fig. 2. FTIR spectra of CO adsorbed on reduced Rh-ZSM-5. Equilibrium pressure of 1730 (a) and 65 Pa (b) and after short evacuation (c).

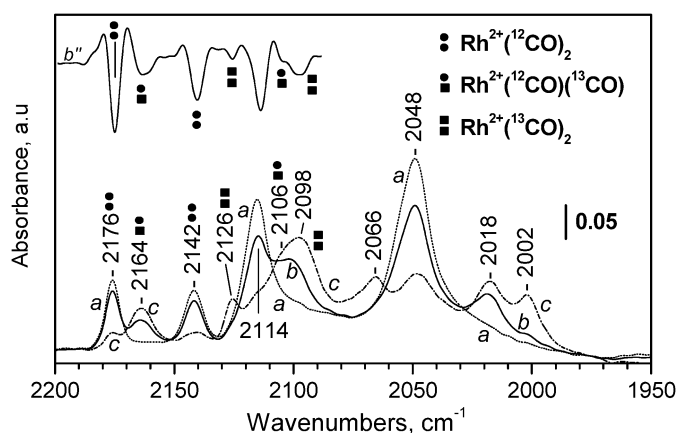


Fig. 3. FTIR spectra of  $^{12}\text{CO}$  and  $^{13}\text{CO}$  co-adsorbed on reduced Rh-ZSM-5. Spectrum taken after evacuation of  $^{12}\text{CO}$  (1730 Pa equilibrium pressure) (a); introduction of 0.22  $\mu\text{mol}$  of  $^{12}\text{CO}$ – $^{13}\text{CO}$  mixture (molar ratio of 1:1) to the sample; equilibrium pressure of 44 Pa  $^{12}\text{CO}$ – $^{13}\text{CO}$  mixture (c). The second derivative of spectrum b is presented as  $b''$ .

rhodium cations in a high oxidation state (most probably  $\text{Rh}^{3+}$ ) [20,26]. To support this assignment, we studied CO adsorption on a sample reduced at 573 K. In this case the bands at 2176, 2142, 2114, and 2048  $\text{cm}^{-1}$  appeared with a slightly reduced intensity after CO adsorption, whereas the band at 2195  $\text{cm}^{-1}$  was absent. This finding is consistent with the reduction of the  $\text{Rh}^{3+}$  sites. In what follows we concentrate on the bands at 2176 and 2142  $\text{cm}^{-1}$ .

The two bands at 2176 and 2142  $\text{cm}^{-1}$  appeared to change simultaneously, suggesting that they characterize one kind of polycarbonylic species. To prove this hypothesis and to establish the exact number of the CO ligands, we studied  $^{12}\text{CO}$ – $^{13}\text{CO}$  coadsorption. The cell was evacuated, after which only the bands arising from  $\text{Rh}^+(\text{CO})_2$  gem-dicarbonyls (at 2114 and 2048  $\text{cm}^{-1}$ ) and those at 2176 and 2142  $\text{cm}^{-1}$  remained in the spectrum (Fig. 3, spectrum a). Then small doses of a  $^{12}\text{CO}$ – $^{13}\text{CO}$  isotopic mixture (molar ratio of ca. 1:1) were successively added into the cell. The first dose of the isotopic mixture provoked a decrease in the intensity of all four carbonyl bands, most pronounced with the bands arising from  $\text{Rh}^+(\text{CO})_2$  species (Fig. 3, spectrum b). In addition, a series of new bands

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