I.R. Spectroscopic Evidence of a Well Defined Rhodium Dicarbonyl in Highly Dealuminated Zeolite Y, formed by Interaction of Carbon Monoxide with Exchanged Rhodium

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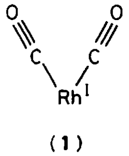
I.r. spectra with unusually sharp (full width at half maximum $\leqslant 5$ cm^{-1}) carbonyl bands and their corresponding ^{13}CO satellites are observed following the interaction of CO with both reduced and oxidized rhodium introduced into dealuminated zeolite Y (US-Ex), indicating the formation of a well defined rhodium(I) dicarbonyl compound with zeolite framework oxygen as ligands.

Over the last few years the interaction of CO with rhodium supported on oxides or introduced into zeolites has attracted considerable attention. In 1957 it was found[1] that this interaction leads to the formation of a geminal dicarbonyl species (**1**) on well dispersed rhodium catalysts.



(**1**)

Recently it was reported[2] that the properties of this species are strongly dependent on the support. For Rh in zeolites, there is some evidence[3—7] that the formation of various dicarbonyl species depends on the zeolite structure (channel size) and the preparation and interaction conditions. In order to investigate the effect of different Si : Al ratios, we have prepared a series of Rh-exchanged zeolites with the same faujasite structure but with different Si : Al ratios. Rh introduced into highly dealuminated zeolite Y (US-Ex) shows some remarkable properties, which we now report.

Rh/US-Ex (1 wt.% Rh, Si : Al 95) was prepared as follows. Zeolite Y was dealuminated by thermochemical treatment of NH_4-Y followed by extraction of the non-framework alumin-

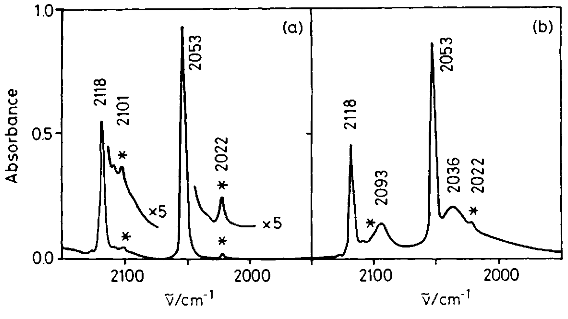


Figure 1. I.r. spectra of Rh/US-Ex in the carbonyl stretching region as the result of interaction with 1.3 kPa of CO at 423 K for 30 min (a) after calcination in air at 673 K, and (b) after calcination in air at 673 K and subsequent reduction with hydrogen at 573 K. The ^{13}CO satellites are indicated by an asterisk. The spectra are corrected for the background.

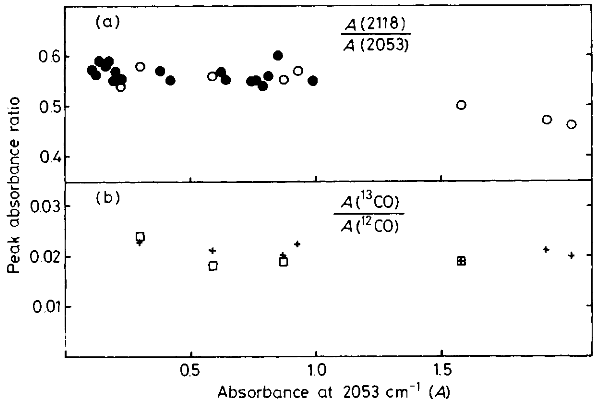


Figure 2. Peak absorbance ratios at different CO coverages: (a): peak absorbance ratio of the bands due to symmetric (2118 cm^{-1}) and antisymmetric (2053 cm^{-1}) stretching of CO adsorbed on (○) oxidized and (●) reduced catalysts; (b): peak absorbance ratio of the ^{13}CO satellites and their parent bands: 2101/2118 (□) and 2022/2053 (+).

ium species with dilute hydrochloric acid.[8] Rh ion exchange was performed by treating the zeolite with an aqueous solution of $[Rh(NH_3)_5Cl](OH)_2$. The dispersion of rhodium was determined by hydrogen chemisorption at room temperature after reduction with hydrogen at 673 K. We found an H : Rh ratio of about 1.2 : 1. The transmission i.r. studies were performed in a conventional glass cell for *in situ* pretreatments. The spectra were recorded on a double-beam Fourier transform i.r. spectrometer (IRF-180, ZWG, Academy of Sciences, G.D.R.) with a resolution of 2 cm^{-1}.

Figure 1 shows some typical examples for the interaction of CO with both reduced and oxidized samples. The following results are of special interest.

First, the main bands due to the CO stretching are unusually sharp. The line width (full width at half maximum, F.W.H.M.) for CO adsorbed on supported transition metals is usually larger than 15 cm^{-1} whereas we always find that the F.W.H.M. for CO on Rh/US-Ex never exceeds 5 cm^{-1}. This indicates the formation of a very well defined carbonyl compound within the zeolite framework.

Secondly, owing to the intensity and sharpness of the bands, the ^{13}CO satellites are well resolved, even for ^{13}CO in natural abundance (1.1%). Analysis of the intensities of the satellite bands indicates a proportion of about 2% relative to the parent bands for a wide range of overall intensities observed at different CO coverages (Figure 2, b). This ratio is as expected for a $Rh^I(CO)_2$ species.

Table 1. Observed and calculated wavenumbers of the symmetric (s) and antisymmetric (as) stretching of the CO groups in $Rh^I(CO)_2$ on US-Ex.

Species		Wavenumber/cm^{-1} Obs.	Calc.[a]
$Rh^I(^{12}CO)_2$	s	2118	(2118)
	as	2053	(2053)
$Rh^I(^{13}CO)(^{12}CO)$	s	2101	2102
	as	2022	2022

[a] k(CO) 1757 N m^{-1}; k(CO–CO′) 55 N m^{-1}.

Using an approximate force field[9] for $Rh^I(CO)_2$ (C_{2v} symmetry) it is possible to calculate the position of the ^{13}CO satellites from the main ^{12}CO bands.[5] Table 1 gives the corresponding values for Rh/US-Ex. The agreement between calculated and observed values supports the assumed C_{2v} structure of the rhodium carbonyl compound (**1**). From the intensity ratio of the two main carbonyl bands (Figure 2, a) we can estimate the bond angle between the two carbonyl groups,[9] and this is about 106°, in agreement with bond angles estimated for dicarbonyls in Rh/NaY.[5]

Thirdly, the same rhodium(I)–dicarbonyl species is formed starting both from the reduced and from the oxidized samples. The main difference is due to the formation of an additional rhodium carbonyl species on reduced Rh/US-Ex with CO stretching bands at 2093 and 2036 cm^{-1} overlapping in part with the ^{13}CO satellite bands (Figure 1, b). Their wavenumbers indicate that these species are probably formed at the outer surface of the zeolite.[2] The bands at 3631 and 3567 cm^{-1}, which are due to the acid hydroxy groups in the US-Ex framework, can be found after reduction of rhodium, but they disappear during the formation of the dicarbonyl species. This observation supports the suggestion on the role of hydroxy groups in the formation of $Rh^I(CO)_2$ on reduced rhodium catalysts.[10]

The localized charge distribution in highly dealuminated zeolites promotes the formation of well defined structures near the remaining aluminium sites. Two framework oxygen atoms near the aluminium atom are probably co-ordinated to the Rh^I ion, thereby completing the expected four-fold co-ordination of a d^8 cation. The US-Ex framework acts, moreover, not only as a bidentate ligand but also, at the same time, as a matrix leading to effective isolation of the Rh sites.

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