Infrared spectroscopic detection of Rh(1) by CO in supported Rh catalyst

Frigyes Solymosi, János Raskó and Julia Bontovics

Reaction Kinetics Research Group of the Hungarian Academy of Sciences
and Institute of Solid State and Radiochemistry [1]*, University of Szeged,*
PO Box 168, H-6701 Szeged, Hungary

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The detection limit of Rh(1) in the Rh/Al_2O_3 catalyst in a form of $Rh^1(CO)_2$ was determined by FTIR spectroscopy. It was demonstrated that at least 0.5 µg Rh, corresponding to 0.005 wt% of Rh, can be identified in this way. During synthesis gas conversion the predominant surface species is Rh_x–CO, but a detectable amount of Rh(1) exists on the catalyst up to 473 K.

Keywords: Detection of Rh(1); supported Rh catalyst; structural changes of Rh cluster; syngas reaction over Rh; alcohol synthesis; infrared spectrum of adsorbed CO

1. Introduction

This work was initiated by the discussion of the paper by Joyner et al. at the Catalysis Congress in Budapest [1–3]. The paper dealt with the synthesis of oxygenated compounds on Rh/Al_2O_3, characterized by EXAFS measurements. The discussion was concerned with the presence in the catalyst of Rh(1). It was earlier assumed that Rh(1) provides the active centers in methanol synthesis [4] which could be present either due to incomplete reduction of Rh(III) salts, or due to the oxidation of highly dispersed Rh metal by the reacting system, or due to a charge transfer process between the rhodium cluster and the support. It was pointed out that, although the EXAFS technique is the most powerful method for determination of the structure of supported metals and their coordination, it is far too insensitive to detect small quantities of isolated Rh atoms or ions [2]. It was argued that FTIR spectroscopy is a much more sensitive technique in the detection of Rh(1) in the form of $Rh^1(CO)_2$ species [2]. An other advantage of FTIR is that it can be applied as an in situ method. The response included the remark that "the advantage

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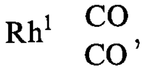
[1] This laboratory is a part of the Center for Catalysis, Surface and Material Science at the University of Szeged.

of EXAFS is that it gives a true average of the species present in the sample, in comparison to infrared, where quantification is rarely attempted" [3].

In the present work an attempt is made to determine the minimum amount of $Rh^1(CO)_2$ detectable on Al_2O_3 by registering its infrared spectrum. The basis of this study is that (i) the adsorption of CO completely disrupts the small Rh clusters on Al_2O_3 to isolated Rh(0) atoms, (ii) the isolated Rh(0) is oxidized to Rh(1) by the OH groups of the support and (iii) CO forms a dicarbonyl species,



$$\mathrm{Rh}^1\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix},$$

which gives rise to two intense absorption bands at ~ 2100 and ~ 2030 cm^{-1}, assigned to asymmetric and symmetric CO stretchings [5–10].

2. Experimental

Rh/Al_2O_3 samples were prepared by incipient wetting of Al_2O_3 (Degussa) with an aqueous solution of $RhCl_3 \cdot 3H_2O$ (Johnson–Matthey). After impregnation, the samples were dried in air at 373 K. For IR studies, the dried Rh/Al_2O_3 powder was pressed into self-supporting wafers (30 × 10 mm, 10 mg/cm^2). The pretreatment of samples was performed in a vacuum IR cell: the samples were (a) heated (20 K/min) to 573 K under continuous evacuation; (b) oxidized with 100 Torr of O_2 (133.3 Pa) for 30 min at 573 K; (c) evacuated for 15 min; and (d) reduced in 100 Torr of H_2 for 60 min at 573 K. This was followed by degassing at the same temperature for 30 min and by cooling the sample to room temperature. CO (10 Torr) was admitted on the sample at 300 K. The gases were circulated during oxidation, reduction and catalytic reaction.

An in situ IR cell was used which permitted IR spectra to be taken in the temperature range 100–573 K. Infrared spectra were recorded with a BIORAD (Digilab. Div.) Fourier transform IR spectrometer (FTS 7) with a wavenumber accuracy of ± 2 cm^{-1}. Typically, 16 scans were registered. All subtractions of the spectra in the present work involved a subtraction factor of 1.0000.

3. Results and discussion

Fig. 1 presents IR spectra recorded after the adsorption of CO at different Rh contents. Following CO admission into the cell at 300 K, intense absorption bands appeared immediately at 2090–2100 and 2020–2030 cm^{-1}. Their positions and intensities did not change when the adsorption time was increased from 1 min to 25 h. This suggests that the CO (and OH)-induced transformation of the Rh_x crystallites to Rh(1) species [5–10] occurred very rapidly at 300 K in these highly dispersed samples. The intensities of the dicarbonyl bands gradually decreased with decrease of the amount of Rh. There was no or only a slight spectral indication of

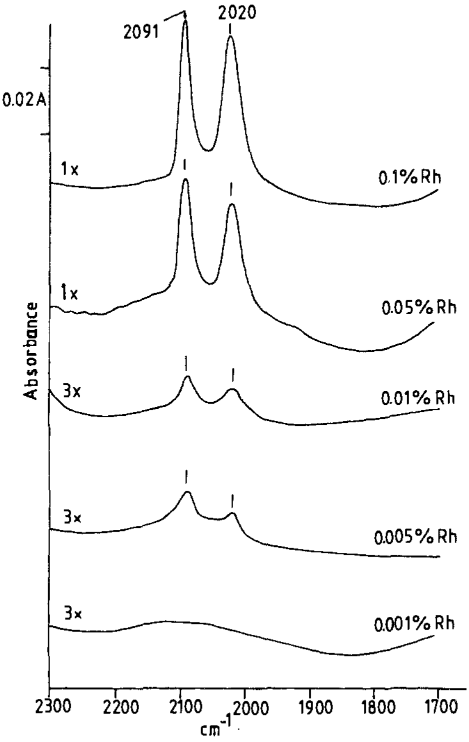


Fig. 1. IR spectra of adsorbed CO on Rh/Al_2O_3 at 300 K for different Rh contents.

the presence of either linearly bonded CO (absorbing at 2026–2066 cm^{-1}, depending on the coverage) or bridge bonded CO (absorbing at $\sim$ 1850 cm^{-1}), which would indicate the presence of undisrupted Rh_x crystallites. If it is assumed for a moment that all the Rh deposited on the Al_2O_3 is available for CO adsorption and the whole is transformed into Rh(1), the lowest amount of Rh(1) detected in this way (using 10 mg/cm^2 pellet) is 0.5 μg Rh which corresponds in the present case to a catalyst Rh content of 0.005%.

In fig. 2 the integrated absorbances of the dicarbonyl bands are plotted versus the Rh content of the sample. Straight lines were obtained which intercepted the abscissa at about 0.2 μg Rh. To explain this result, it might be speculated that this small amount of Rh is lost during the preparation [11]. As Rh is strongly bonded to alumina at such a low concentration, we can exclude the evaporation of this Rh at the relatively low temperature ($\sim$ 573 K) of oxidation and reduction of the Rh/Al_2O_3 sample. It is more probable that a small proportion of the Rh diffuses inside the pore structure or into the alumina surface layer.

It was previously observed that at higher temperatures CO induces the reductive agglomeration of Rh(1) and the reformation of Rh_x [6],

$$2\,\mathrm{Rh}^1 \begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix} + \mathrm{O}^{2-} = \mathrm{Rh_2{-}CO} + \mathrm{CO_2} + \mathrm{CO}\,,$$

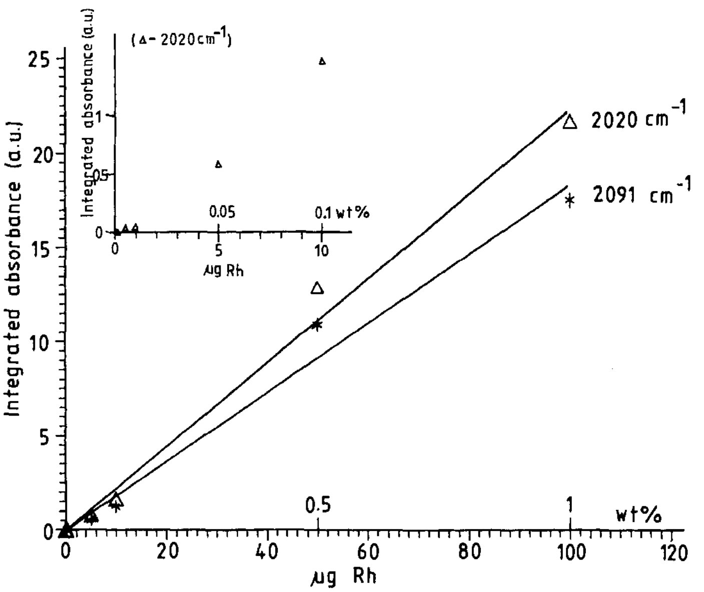


Fig. 2. Integrated absorbances of absorption bands of $Rh^1(CO)_2$ as a function of Rh content (μg and wt%) of Rh/Al_2O_3 samples. The amount of Rh (μg) is related to 10 mg/cm^2 of Rh/Al_2O_3 pellet.

and the addition of hydrogen to the CO promotes the CO-induced reductive agglomeration of Rh(1) [7]. Accordingly, it is a crucial question whether Rh(1) exists on the catalyst during synthesis gas conversion, and can be detected in the presence of a large amount of Rh_x crystallites.

In the next experiment we followed the spectral changes of 1% Rh/Al_2O_3 (T_R = 573 K) in the presence of a H_2 + CO (1 : 1) gas mixture at gradually increasing temperatures (fig. 3). Note that the reaction between CO and H_2 on Rh/Al_2O_3 sets in above 423 K. As a result, the gas composition over the catalyst changes, one of the products being water, which is advantageous for the formation of Rh(1) [6]. At lower temperatures, 300–423 K, intense dicarbonyl bands dominated the IR spectra, indicating the presence of Rh(1) species under reaction conditions. Above 423 K, however, the absorption band of linearly bonded CO also appeared, the intensity of which gradually increased with lengthening of the reaction time and with elevation of the temperature. At the same time, the dicarbonyl bands attenuated. The highest temperature at which Rh(1) in the form of $Rh^1(CO)_2$ could be detected by means of magnified difference spectra was 473 K. This relates to the detection of the ~ 2100 cm^{-1} band, as the low-frequency band of the dicarbonyl species cannot be distinguished from the growing band of Rh_x–CO. It is important to point out that the absence of $Rh^1(CO)_2$ species under these conditions is not due to the desorption of CO from Rh(1), as the dicarbonyl bands were missing

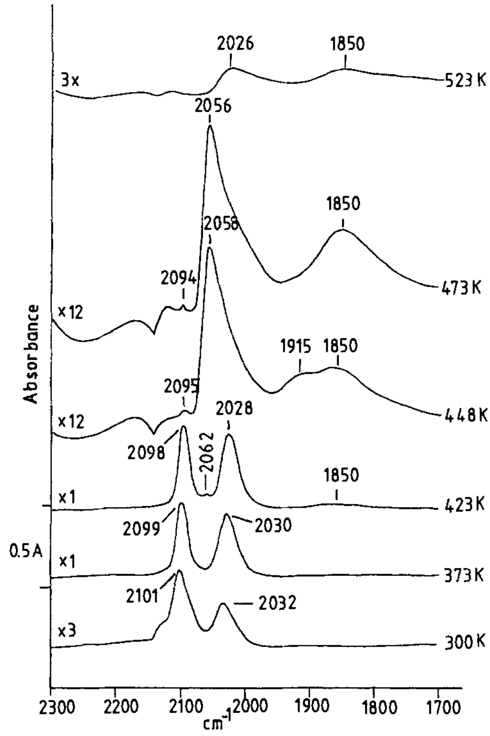


Fig. 3. IR spectra of adsorbed CO in the presence of H_2 + CO (10 Torr each) at different temperatures. The sample contained 1 wt% Rh.

even when the catalyst sample was rapidly cooled from 523 K to 100–120 K in the presence of reacting gas mixture.

The catalytic performance of Rh catalyst is markedly influenced by the nature of the promoter. One of the more efficient promoters in the production of alcohol from synthesis gas is CeO_2 [12], which greatly stabilizes the Rh(1) against reductive agglomeration at high temperatures, even in the presence of hydrogen [13]. Accordingly, there is a good possibility that on the promoted catalyst Rh(1) exist, in a low, but sufficient concentration under the reaction conditions, and can provide active centers in the synthesis of alcohol and other oxygenated compounds.

4. Conclusion

In conclusion we may state that the presence of Rh(1) in Rh/Al_2O_3 catalyst can be sensitively detected in the form of $Rh^1(CO)_2$ by FTIR spectroscopy during the catalytic reactions involving CO. This could be the case for other supports too, as $Rh^1(CO)_2$ is readily formed on all oxidic supports. The limit of detection and the region of stability of this dicarbonyl species, however, may be influenced by the nature of the support.

Acknowledgement

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