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Infrared Studies of the Effects of Promoters on CO-Induced Structural Changes in Rh

INTRODUCTION

Several new features concerning the interaction between CO and supported Rh have recently been established. EXAFS (*1*) and infrared spectroscopy (*2*) have been used to demonstrate that adsorption of CO on Rh crystallites at 300 K leads to oxidative disruption of the Rh–Rh bonds and to the formation of isolated Rh^1 sites. This was exhibited in the infrared spectrum by the development of the gem-dicarbonyl, $Rh(CO)_2$, absorption bands at 2100 and 2030 cm^{-1} (*2*); traces of H_2O accelerate this process (*2*). At temperatures above 423 K, however, another effect of CO comes into prominence, resulting in the formation of Rh crystallites at the expense of isolated Rh^1 sites, as indicated by the appearance of the band at 2030–2045 cm^{-1}, due to Rh_x–CO (*2*). The oxidative disruption of Rh_x was retarded, while the reductive agglomeration of Rh^1 was accelerated in the presence of H_2 (*3*). The observed influence of hydrogen helped us to explain why only linearly bonded CO is formed in surface reactions (e.g., the H_2 + CO_2 interaction, HCOOH and HCOH decomposition) on highly dispersed Rh, on which CO adsorption otherwise produced gem-dicarbonyl immediately at 300 K (*4*). Several of the above findings have been observed in recent studies of Rh supported on zeolite (*5*) and alumina (*6*).

Kiennemann *et al.* (*7*) have recently demonstrated that the addition of CeO_2 to the Rh/SiO_2 catalyst improves the selectivity for ethanol formation in the H_2 + CO reaction. On the assumption that Rh^1 is the site of alcohol formation in the hydrogenation of CO (*8, 9*), it has been envisaged (*10*) that the influence of CeO_2 promoter on the catalytic performance of Rh may be associated with its effects on the oxidative disruption and reductive agglomeration of supported Rh.

The present work is an examination of the CO-induced structural changes in supported Rh, with a consideration of the influence of CeO_2 and K_2O additives.

EXPERIMENTAL

Rhodium samples were prepared by coimpregnation of SiO_2 (Aerosil 200) or Al_2O_3 (Degussa P 110) with an aqueous solution of $Rh(NO_3)_3$ and $Ce(NO_3)_4$, or $Rh(NO_3)_3$ and KNO_3, respectively. After impregnation, the samples were dried in air at 373 K.

For infrared studies, the dried powder was pressed into thin self-supporting wafers (30 × 10 mm, 20 mg/cm^2). The pretreatment of the samples was performed in the vacuum IR cell; the sample was (a) heated (20 K min^{-1}) to 573 K under constant evacuation, (b) oxidized with 100 Torr of O_2 (1 Torr = 133.3 Pa) for 60 min at 573 K, (c) evacuated for 30 min, and (d) reduced with 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 the temperature of the experiment. The gases were circulated during oxidation and reduction processes.

Infrared spectra were recorded with a Specord 75 IR double-beam spectrometer (Zeiss, Jena) with a wavenumber accuracy of ±5 cm^{-1}. In certain cases difference spectra were produced and magnified with the help of a DATA system (Tracor North-

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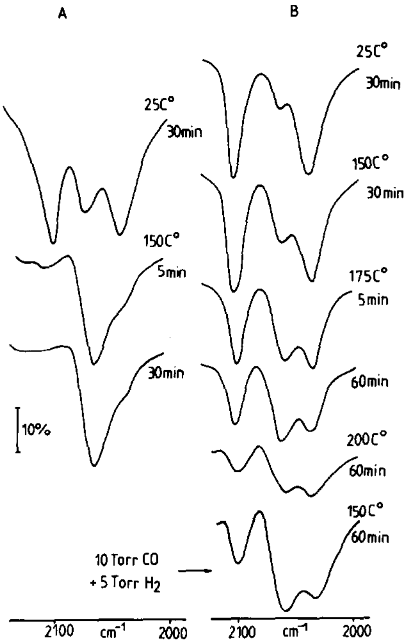

FIG. 1. Infrared spectra of 1% Rh/SiO_2 (A) and 1% Rh+5% CeO_2/SiO_2 (B) in the presence of 10 Torr CO (and H_2 + CO) at different temperatures (the background spectra have been subtracted).

ern, TN 1710) conjugated directly to the Specord 75.

RESULTS AND DISCUSSION

In the study of the effects of support on the topological changes in Rh, it appeared that the oxidative disruption of Rh_x crystallites depends sensitively on the nature of the support; the disruption occurs significantly more slowly on silica than on alumina *(11)*. On the other hand, the reductive agglomeration of Rh^1 sites was found to be faster on silica supports *(11)*.

In Fig. 1A we present the spectral changes observed for 1% Rh/SiO_2 reduced at 573 K, following CO admittance to the sample at 300 K. Strong bands were produced at 2100 and 2040 cm^{-1} even after only a short contact time (~1 min), due to gem-dicarbonyl, which indicates that a significant proportion of the Rh crystallites is disrupted by CO. However, the intense band at 2070 cm^{-1} (CO linearly bonded to Rh_x crystallites) and the very weak one at 1850 cm^{-1} (CO bridge bonded to Rh_x crystallites) also indicate the presence of undisturbed Rh_x crystallites in the sample. After a longer contact time, an increase in the intensity of gem-dicarbonyl (and a simultaneous attenuation of the bands due to CO associated with Rh_x clusters) can be observed, which is a clear indication of the further occurrence of CO-induced structural changes in the Rh. (These changes took place almost immeasurably rapidly at 300 K when the same amount of Rh was used, but on an alumina support.)

A sudden spectral change also occurred in the present case, when the temperature of the sample was raised to 423 K in the presence of CO (Fig. 1A). The intensity of the gem-dicarbonyl bands decreased markedly even in 5 min, and the bands were hardly detectable after 30 min. The linearly bonded CO band at 2065 cm^{-1} became the dominant band, but the band at 1850 cm^{-1} due to bridge-bonded CO was also intensified slightly (not shown in the spectrum).

In the presence of 5% CeO_2 the adsorption of CO at 300 K produced practically the same spectrum as that in the case of the CeO_2-free sample. The intensity ratio of the bands of gem-dicarbonyl and linearly bonded CO ($R = J_{2100}/J_{2070}$) was somewhat higher for the Rh + CeO_2/SiO_2 sample. However, the behavior of this sample was dramatically different from that of the CeO_2-free sample at higher temperatures. As revealed by the spectra presented in Fig. 1B, the $Rh^1(CO)_2$ species exhibited a remarkable stability in this case; at 423 K there was hardly any decrease in the intensity of its infrared band, and the gem-dicarbonyl existed even at 473 K. Since the gem-dicarbonyl is a Rh^1 complex, this result suggests that the reductive agglomeration of Rh^1 into Rh_x clusters is greatly retarded by CeO_2; i.e., CeO_2 promoter markedly stabilizes Rh^1 in the presence of CO. The stabilizing effect of CeO_2 was exhibited in the presence of H_2, also; in this case the absorption bands due to gem-dicarbonyl attenuated somewhat faster, but they were readily detectable even at 448 K (Fig. 1B). The possible reason for the stabilizing effect of the CeO_2 is that it supplies oxygen

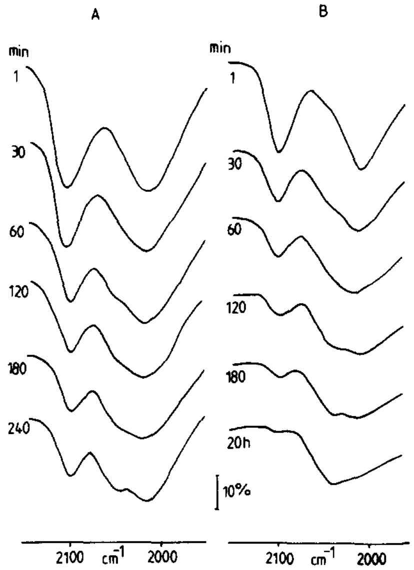

FIG. 2. Infrared spectra of 1% Rh/Al_2O_3 (A) and 1% Rh+1% K_2O/Al_2O_3 (B) in the presence of 50 Torr CO at 448 K.

to the Rh and hence preserves the Rh^1 sites.

Similar studies have been performed to characterize the influence of K_2O (another commonly applied additive for the H_2 + CO reaction) on the CO-induced structural changes in Rh. In this case we used an alumina support.

The oxidative disruption of K_2O-doped and undoped Rh_x occurred almost immeasurably rapidly at 300 K; strong bands due to $Rh^1(CO)_2$ species appeared even after an adsorption time of 1 min, and there was no spectral indication of the presence of Rh_x–CO. A very weak band due to bridge-bonded CO was detected at 1850 cm^{-1}.

A significant difference between the K_2O-doped and the K_2O-free samples was exhibited at 448 K (Fig. 2). In the case of Rh/Al_2O_3, the reductive agglomeration of Rh^1 took place slowly at this temperature, as indicated by the development of the band at 2045 cm^1 due to Rh_x–CO and by the gradual decrease in the intensity of the $Rh^1(CO)_2$ species (Fig. 2A). This process occurred appreciably faster in the presence of 1% K_2O, as can be seen in the spectra in Fig. 2B. Accordingly, potassium additive—very likely due to an electronic effect—promotes the CO-induced reductive agglomerization of Rh^1, i.e., the reformation of Rh_x clusters from isolated Rh^1 sites. In some respect similar effects of K_2O were reported for a 0.5% Rh/Al_2O_3 film by Dai and Worley (*12*) at a CO background pressure of 1×10^{-3} Torr. However, in this case the potassium additive—very likely due to the low CO pressure—promoted the desorption of the gem-dicarbonyl and not its transformation into Rh_x–CO species.

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