

SURFACE SCIENCE LETTERS

DISSOCIATION OF CO ON SUPPORTED Rh

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The adsorption and dissociation of CO have been investigated on alumina supported Rh at atmospheric pressure. The dissociation of CO was detected above 473 K. The carbon formed reacted with H₂ even at 300–473 K yielding CH₄. A significant aging of surface carbon occurred above 573 K.

There is a certain controversy in the literature as concerns the dissociation of CO on Rh surfaces. Sexton and Somorjai [1] have reported that heating Rh foil in CO results in the production of appreciable quantities of surface carbon and oxygen; these recombine to give CO_(g), which desorbs near 1000 K, far above the desorption temperature of undissociated CO. The dissociative adsorption of CO has been observed at low pressures on the Rh(331) and (755) surfaces [2].

On the other hand, Yates et al. [3] have raised some questions about the probability of CO dissociation on Rh surfaces. Using the combined method of Auger electron spectroscopy, isotope exchange and thermal desorption spectroscopy, they have shown that the probability of dissociation of CO on the Rh(111) surface at 300–870 K is negligible compared to the probability of molecular desorption [3,4], and concluded that CO adsorbs predominantly molecularly on Rh at low pressures, even on polycrystalline and stepped surfaces of Rh [4].

Somorjai et al. [5], however, disagreed with this conclusion and demonstrated that at elevated temperatures CO can dissociate on Rh surfaces containing irregularities (steps, kinks and defects). The adsorption and decomposition of CO on Rh surfaces have been recently investigated using field emission microscopy [6]. Thermal dissociation of CO was not detected on clean Rh surfaces at pressures up to 10⁻¹ Torr and temperatures below 1000 K.

This controversy has prompted us to report our results related to the dissociation of CO on supported Rh. It appears that whereas a reasonable number of studies have dealt with the problem of the dissociation of CO on Rh single-crystal surfaces, very little attention has been paid so far to this problem on supported Rh.

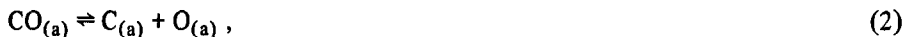
From the ir spectra of adsorbed CO on supported Rh, Primet [7] drew some indirect conclusions with regard to the dissociation of CO. From the appearance of

the twin CO band in the spectra of Rh/Al₂O₃ and RhNaY samples, he inferred that the CO undergoes dissociation on these surfaces even at or above 183 K, and that gem dicarbonyl is formed on oxidized Rh, probably Rh^I. However, no evidence for the oxidation of Rh via CO dissociation below 300 K was found by Yates et al. [8]. They suggested that the twin CO is formed on isolated Rh sites, and that this occurs rapidly via an activated process above 200 K.

As supported Rh is an effective catalyst in the hydrogenation of CO and CO₂ [9–13], the question of the dissociation of CO is highly relevant to the elaboration of the mechanism of these reactions.

The dissociation of CO was investigated first in a microcatalytic pulse system described elsewhere [11,14,15]. Small amounts of CO (one pulse contained 41.6 μmol CO) were injected into the He flowing over Rh/Al₂O₃ previously reduced at 673 K. The products were analyzed with a Hewlett-Packard gas chromatograph equipped with an electronic digital integrator.

The results are shown in fig. 1. If we accept that CO₂ is formed in the reaction sequence



and that reaction (3) is fast, then the amount of CO₂ found may represent the dissociation of CO. In order to avoid the disturbing effect of water and the occurrence of the water–gas shift reaction, all the gases were very carefully dried with a molecular sieve at the temperature of liquid air. The reduced catalyst sample was evacuated at 673 K for several hours before CO injection.

It appears that when the reduced Rh/Al₂O₃ was subjected to 1 CO pulse at 473 K, only a small fraction of the CO underwent dissociation (the ratio of surface C to the number of surface Rh atoms, C/Rh_s, was ~0.025); however, the extent of dissociation increased considerably as the temperature was raised (fig. 1).

In the subsequent measurements the surface carbon formed was reacted with H₂. The adsorbed CO was removed in a dry He flow at 523–548 K, until the ir spectroscopic measurements revealed no sign of bands due to adsorbed CO. In most cases this required 15–20 min. Calculations based on gravimetric and ir spectroscopic measurements showed that the minimum amount of adsorbed CO detectable by ir spectroscopy is 2–3 μmol/g. The limit can be decreased to about 0.2 μmol/g by using an ordinate extension unit.

When H₂ pulses were admitted onto the sample treated with CO at 473–573 K, small amounts of CH₄ were obtained even at 298 K, and much more at 373 K and higher temperatures (fig. 1). The total amount of carbon obtained as CH₄ was less than the amount deposited. It is an important observation that the adsorbed CO (the adsorption temperature was below 373 K) can not be hydrogenated to CH₄ at 373–423 K.

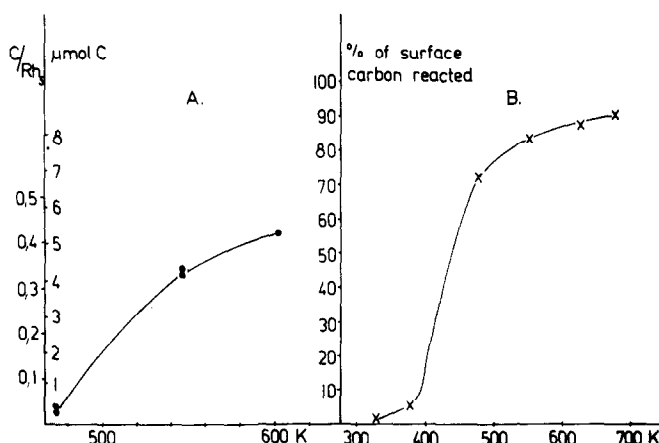


Fig. 1. (A) The amount of surface carbon formed after exposure of 1% Rh/Al₂O₃ to 1 CO pulse (41.6 $\mu\text{mol CO}$) at different temperatures. The amount of carbon was calculated from the amount of CO₂ evolved. The surface Rh content of 1% Rh/Al₂O₃ determined by H₂ adsorption was 32.2 $\mu\text{mol/g}$ catalyst. The weight of the sample was 0.39 g. (B) The maximum amount of surface carbon transformed into CH₄ in the reaction with H₂ at different temperatures. The surface carbon was produced by subjecting 1% Rh/Al₂O₃ to 10 CO pulses (one pulse contains 41.6 $\mu\text{mol CO}$) at 548 K.

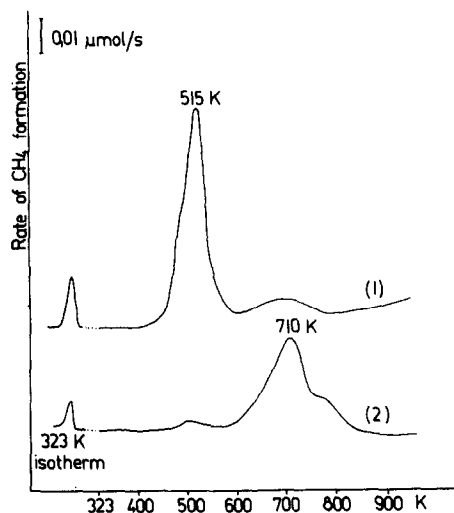


Fig. 2. TPR spectra with H₂ following carbon deposition by exposure of 1% Rh/Al₂O₃ to 5 CO pulses at 548 K (1) and 603 K (2). Heating rate was 40 K min⁻¹.

The reactivity of surface carbon was further investigated by temperature-programmed reaction spectroscopy. The results revealed that different kinds of surface carbon are produced by CO dissociation similarly as in the case of Ni [16]. The more reactive form reacts with H₂ at 300–320 K, and the less reactive one only above 600 K (fig. 2). The ratios of the surface carbon species depend on the temperature of their production, as well as on their thermal treatments. This can very probably be attributed to the transformation of carbidic carbon into the less reactive graphitic form.

In conclusion we can state that CO does dissociate on supported Rh; the dissociation can be detected above 473 K. The extent of dissociation, however, is much less than on supported Ni, Co, and Fe [15–18]. A significant aging of surface carbon occurs above 573 K.

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