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The Coadsorption of CO and H_2 on Silica-Supported Ru Catalysts

In reviewing the catalytic literature on methanation, one cannot help but be struck by the unusually high specific activity of supported Ru for this reaction. Vannice (*1*) measured the turnover number for methane formation on Ru–SiO_2 catalysts at 275°C and found it to be 181×10^{-3} molec. site^{-1} sec^{-1}. The next most active catalyst was Fe–SiO_2 with a turnover number of 57×10^{-3} molec. site^{-1} sec^{-1}. The magnitude of this turnover number has been questioned by some, however, we have obtained results in substantial agreement with those reported by Vannice (*2*).

It is generally agreed that the dissociative adsorption of CO is an important first step in the reaction between CO and H_2 to form methane. Surface carbon atoms which form as a result of the disproportionation of CO are then rapidly hydrogenated to form methane and Fischer–Tropsch reaction products. Catalysts such as Pt and Pd which do not readily dissociate CO are poor methanation catalysts. From these observations, we might, therefore, conclude that Ru is the most active group VIII metal in promoting the disproportionation of CO. The results of Rabo *et al.* (*3*) are in conflict with this reasoning. These authors studied the disproportionation of CO over several supported group VIII metals including Pd, Co, Ru, and Ni. In these studies measured pulses of CO were passed over the catalysts at 300°C and the resulting carbon layer was quantitatively determined from a knowledge of the CO_2 which was formed. Cobalt was found to be the most active metal in promoting carbon formation followed closely by Ni. The activity observed for Ru was considerably less than that for Co or Ni but it was still much larger than that observed for Pd. It is apparent from these observations that the dissociative capacity of the group VIII metal cannot by itself explain the very large methanation rate observed on Ru. Other possibilities to be considered include (i) the formation of surface complexes, (ii) the nature of the binding states of surface carbon, (iii) the rate at which the CO bond is cleaved over the group VIII metals, and (iv) variations in the surface adlayer induced by the coadsorption of H_2 and CO. In this communication we will report on the latter, that is, the coadsorption of H_2 and CO on silica-supported Ru catalysts.

The flow system used in this study has been described in detail elsewhere (*4*). However, it enables use of the reactor as either a pulse microreactor or a single pass differential reactor. An important feature associated with this system is that the microreactor could be substituted for by an infrared cell which could also double as a single pass differential reactor. The infrared cell-reactor was designed in such a way as to ensure that the reactants passed through the sample disc with little or no leakage occurring around the edges of the sample.

The silica-supported catalysts used in this study were prepared by impregnation. Initially, the appropriate weight of Ru $Cl_3 \cdot 3H_2O$ (Strem Chemical) was dissolved in an amount of deionized water sufficient to ensure the complete wetting of the silica support. The solutions were mixed with Cab-o-sil, grade M-5 (Cabot Corp., Boston, Mass.), until a slurry having the consistency of a thin paste was formed. The slurry was dried in a vacuum desiccator at room temperature for 1 or 2 days and stirred regularly to retain uniformity. The dried catalyst was ground into a fine powder before use. Total metal loading was 0.3 mmole/g support. For use in the spectroscopic reactor, the dried catalyst was pressed into self-supporting discs 25 mm in diameter with an optical density of approxi-

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mately 25 mg/cm^2. All infrared spectra were recorded on a Perkin-Elmer model 281 infrared spectrophotometer which was interfaced with a Perkin-Elmer data station. Chemisorption measurements were performed using the dynamic pulse method (*5*). These measurements could be performed either in the microreactor or directly in the infrared cell-reactor.

The gases used in this study were all research grade or better and were subjected to further purification using standard techniques previously described (*2*). Because chemisorption results obtained using the dynamic pulse method are extremely sensitive to trace amounts of H_2O and O_2 in the carrier gas stream, care was taken to exclude these contaminants from the catalyst sample. The oxygen concentration in the carrier gas at the sample was measured and found to be about 0.1 ppm. Water levels were much lower.

A fresh catalyst was treated as follows: evacuated at 400°K for 1 hr, temperature increased in flowing H_2 from 400 to 600°K at about 10°C/min, reduced in flowing H_2 (25 ml/min) at 600°K for 2 hr, followed by evacuation at 720°K for 30 min. The purpose of evacuating the catalyst at a higher temperature than that used in the reduction, was to ensure the dehydroxylation of the support and thus reduce traces of H_2O which might interfere with the adsorption. The microreactor containing about 300 mg of the catalyst was then isolated from the pretreatment vacuum system by means of two four-way stopcocks and transferred to the reaction flow system. Prior to a chemisorption experiment, the temperature of the catalyst was increased in flowing H_2 to 600°K at 10°C/min and reduced in flowing H_2 (25 ml/min) at 680°K for 2 hr followed by treatment in flowing He for 1 hr and cooling to room temperature in flowing He.

Each sample disc was subjected to the following pretreatment schedule prior to final positioning in the infrared cell: heating in flowing H_2 at 400°K for 1 hr, temperature increased in flowing H_2 from 400 to 600°K at 10°C min^{-1} and reduced in flowing H_2 (25 ml/min^{-1}) at 600°K for 2 hr. The sample disc was then cooled to room temperature and positioned in the sample compartment of the infrared cell. The catalyst was then rereduced in flowing H_2 (25 ml/min at 523°K for 2 hr).

Chemisorption Measurements

The adsorption of CO on a silica-supported Ru catalyst using the dynamic pulse technique in a He carrier gas flow stream was measured at 300°K. The volume of CO required to saturate the surface was found to be 38.4 μmole/g of catalyst. In a previous study (*2*), we reported that a stoichiometric ratio of CO : Ru(s) of 1.2 was satisfactory in order to determine Ru surface areas. This is generally consistent with other results reported in the literature. However, the stoichiometry of the CO adsorption on Ru is far from being a precisely defined quantity due to the possibility of multiple adsorption which in turn appears to be dispersion dependent (*6–8*). When the experiment was repeated using pulses of synthesis gas (H_2/CO = 3) rather than pure CO, the volume of CO required to saturate the surface was 107.4 μmole/g of catalyst, or a 2.8-fold increase in the total CO chemisorption. Because of these results, the adsorption of CO was repeated using pulses of CO in a H_2 carrier gas. The results duplicated those obtained using pulses of synthesis gas. For the sake of completeness, the identical series of experiments were performed on a silica–Pt catalyst having the same metal loading as the silica–Ru catalyst studied. The CO uptake was found to be 95.6 μmole/g in He and 100.4 μmole/g in a H_2 carrier gas. Similar results were found on a silica–Co catalyst implying that the enhanced CO adsorption in H_2 appears to occur on Ru but not significantly on Pt or Co. These chemisorption results are summarized in Table 1. In view of these observations, it would seem logical to consider the possibility of the formation of a surface complex involving CO and H_2. Such surface complexes, as possi-

TABLE 1

Summary of Chemisorption Measurements

Catalyst[a]	CO adsorption (μmole/g) in He	CO adsorption (μmole/g) in H_2	$(CO)_{H_2}/(CO)_{He}$	Dispersion
Ru–SiO_2	38.4	107.4	2.8	13.2[b]
Pt–SiO_2	95.6	100.4	1.05	38.3[c]
Co–SiO_2	14.0	18.0	1.28	3.0[d]

[a] Metal loading = 0.3 mmole/g of catalyst.
[b] Measured using CO chemisorption at 300°K.
[c] Measured using H_2 chemisorption at 300°K.
[d] Based on CO adsorption.

ble reaction intermediates, have been suggested by others and several excellent reviews have appeared on this subject (*9*, *10*). However, the structures of these complexes have eluded spectroscopic identification. For this reason, it seemed appropriate to repeat the pulsed chemisorption experiments in the infrared cell-reactor. The results, shown in Fig. 1, duplicate those obtained in the microreactor. It is also clear that a surface complex is not formed as a result of the coadsorption of CO and H_2. Following chemisorption of CO in He, the carrier gas stream was switched to H_2. The position of the infrared absorption band assigned to the stretching vibration of CO centered at 2025 cm^{-1} decreased to 2010 cm^{-1} without a corresponding change in the absorbance. This result shows that the CO extinction coefficient does not depend on the coadsorption of H_2 and CO. When additional pulses of CO were added, both the absorbance and the wavenumber corresponding to the CO stretching frequency increased. The increase in the absorbance was a linear function of the CO chemisorption strongly suggesting the presence of a single chemisorbed species. Multiple adsorption of a twined CO species similar to that reported on Rh(I) (*11*, *12*) is unlikely due to the absence of the symmetric and antisymmetric stretching vibrations.

In our view, the shift in the position of the CO stretching frequency provides the key to an understanding of the observed results. In a previous study (*13*), we reported that the addition of H_2 to CO chemisorbed on the surface of silica-supported Pt–Ru bimetallic clusters resulted in a much larger shift in the position of the CO stretching band corresponding to CO adsorbed on the Ru surface sites. The position of the Pt–CO band was not significantly changed by the addition of H_2. Eischens and Pliskin (*14*) and more recently Stoop *et al.* (*15*) have concluded on the basis of ^{12}CO–^{13}CO adsorption studies on Pt and supported Pt–Cu bimetallic clusters, that dipole–dipole interactions are mainly responsible for observed CO frequency shifts with surface coverage. In a recent study, Cant and Bell (*16*) have shown that the H_2–D_2 exchange reaction over a supported Ru catalyst having a monolayer of chemisorbed CO is only slightly inhibited by the presence of adsorbed CO. On the other hand, Sarkany and Gonzalez (*5*) have shown that the adsorption of H_2 is completely suppressed on a Pt catalyst having a monolayer of chemisorbed CO. These results suggest that the role of the H_2 is to uncouple the CO dipole–dipole interactions through a strong positive interaction between chemisorbed CO and adsorbed H atoms. This is followed by the restructuring

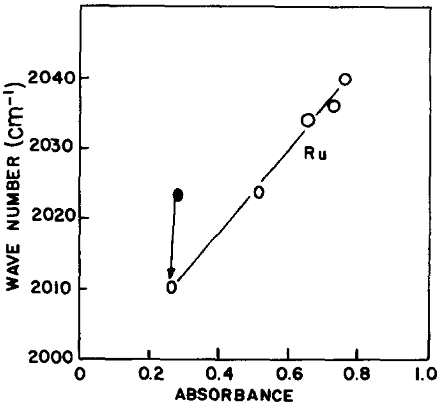

FIG. 1. Frequency of the ir absorption band vs absorbance for the adsorption of CO on silica-supported Ru catalysts at 300°K. ●, In flowing He; ○, in flowing H_2.

of the CO adsorbate layer to form a surface structure which minimizes the CO–CO repulsive energy. Because of the net decrease in the CO–CO repulsive energy, this readjusted CO adlayer can accommodate additional CO. As the surface concentration of CO is subsequently increased through the further addition of CO pulses, the wavenumber corresponding to the position of the CO band is increased to a value of 2040 cm^{-1}, corresponding to the new monolayer. Because the position of the CO stretching band is now 15 cm^{-1} higher than that observed in flowing He, it must be concluded that the CO dipoles are more effectively coupled due to the compaction of the CO adlayer.

In order to compare the binding states of CO adsorbed in a H_2 carrier to those adsorbed in a He carrier, a temperature-programmed desorption (TPD) study was performed. The TPD plots, shown in Fig. 2, were obtained in flowing He (25 ml/min) as the temperature was linearly increased from 300 to 750°K at a rate of 10°K/min. The most important feature of these TPD plots is that no new adsorption states appear to be populated when CO is coadsorbed in the presence of H_2. Although comparisons between TPD studies performed on porous powder and those obtained on single crystals must be made with care, the results of this study are in qualitative agreement with results from the single crystal literature. Peebles *et al.* (*17*) found two desorption maxima in the thermal desorption of CO from Ru(001). These maxima were centered at 406 and 460°K, respectively, compared to 405 and 473°K obtained in this study. A smaller high temperature maxima centered at 698°K was also observed in agreement with TPD studies reported by others on alumina (*18*) and silica-supported Ru (*19*). This high-temperature desorption maxima was not observed in the single crystal studies. As in the single crystal studies, the intensity of the low-temperature maxima increased with increasing CO surface coverage confirming previous studies (*17*) which assign the low-temperature desorption maxima to an adsorbed CO species having strong CO–CO repulsive interactions. An additional feature observed in the TPD spectrum of the H_2 assisted CO adsorption was the formation of small but measureable amounts of

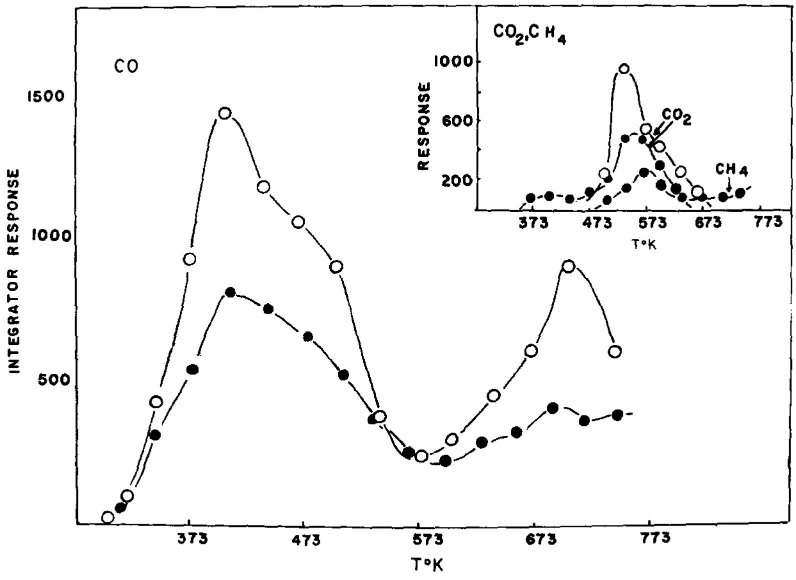

FIG. 2. TPD spectra of CO, CO_2, and CH_4 on silica-supported Ru catalysts. ●, CO adsorbed in flowing He; ○, CO adsorbed in flowing H_2.

CH_4. Methane formation was observed simultaneously with the appearance of CO_2 in the desorption products. This result shows that the catalyst is capable of retaining sufficient amounts of adsorbed hydrogen at 573°K to hydrogenate the carbon atoms formed by the disproportionation of CO. The additional CO_2 observed in the TPD spectrum of the H_2 assisted CO adsorption strongly suggests that the CO–H interaction weakens the CO bond in such a way as to enhance the disproportionation of CO. A similar conclusion has recently been reached by Mori *et al.* (*20*) in CO hydrogenation studies over supported Ni. These authors observed an inverse isotope effect which led them to postulate the formation of a very short-lived enol intermediate which immediately decomposed to form carbon atoms, CO_2 and H_2O.

It is useful to consider the results reported here in connection with what is known concerning adsorbed CO layers on Ru single crystals. Williams and Weinberg (*21*) have shown that when CO is adsorbed on Ru(001) at 110°K, a $(\sqrt{3} \times \sqrt{3})$ R 30° LEED pattern is obtained. In this configuration, CO is adsorbed on "on top" sites. For CO surface coverages greater than $\theta = \frac{1}{3}$, a $(2\sqrt{3} \times 2\sqrt{3})$ R 30° LEED pattern is obtained in which the adsorbed CO has shifted to occupy bridging sites. At still higher CO surface coverages, a $(5n\sqrt{3} \times 5n\sqrt{3})$ R 30° LEED compression pattern is obtained. These results appear to be inconsistent with our infrared results which do not show the presence of any bridge-bonded CO absorption bands in the 1800–1900 cm^{-1} region of the spectrum. However, Pfnür *et al.* (*22*) using a simultaneous ir reflection–absorption and LEED study obtained only one infrared band in the 2000–2060 cm^{-1} region of the spectrum regardless of whether the CO occupied "on top" sites or bridging sites. Work function (*23*), photoemission (*24*), and electron energy loss measurements (*25*) indicate that there is no abrupt change in the binding state of CO on Ru(001) as the coverage increases beyond $\theta = \frac{1}{3}$. Shifts in the position of the adsorbed CO molecules occur in such a way as to minimize CO–CO repulsive interactions. The absence of infrared absorption bands due to bridging CO can be explained by invoking the rehybridization of metal orbitals without the need to invoke the population of a different CO adsorbed state (*22*).

The results of the present study are, therefore, in qualitative agreement with single crystal studies. The coadsorption of hydrogen and CO decreases the CO–CO repulsive interactions enabling the adsorption of additional CO. CO–H positive interactions have also been observed by McKee (*26*) on polycrystalline Ru and by Goodman *et al.* (*27*) on Ru single crystals. Thermal desorption studies of hydrogen adsorbed on Ru(001) in the presence of CO show a noticeable shift in the position of the H_2 desorption maxima to higher temperature (*27*). Wedler *et al.* (*28*) have shown that in the presence of H_2 the capacity of Ni films for CO uptake at 353°K in comparison with the uptake for CO on clean Ni films is doubled. However, they did not find an increase in H_2 assisted CO adsorption at 273°K.

These observations were not limited to room temperature chemisorption measurements. The infrared spectra of the adsorbed species were obtained under reaction conditions. The absorbance of chemisorbed CO at 200°C increased by a factor of about 2 when a CO–He gas stream was switched to one containing the synthesis gas mixture.

In conclusion, we have presented evidence which shows that the surface concentration of CO on silica-supported Ru catalysts increased by a factor of about 3 due to the presence of coadsorbed H_2. We have suggested that a significant reconstruction of the CO adlayer is occurring under reaction conditions by virtue of the presence of the coadsorbed reactant species. We have also shown that a surface complex between CO and hydrogen is an unlikely explanation for the enhanced catalytic activity of supported Ru catalysts in the methanation reaction although the CO–H interaction may enhance catalytic activity by assisting in the disproportionation of adsorbed CO. It is not yet possible to explain with certainty the unusual properties of Ru in the CO + H_2 reaction. However, it may be that H_2 and CO interact more effectively on metals for which the heats of adsorption of CO and H_2 are comparable. Pt and Pd, for example, adsorb CO so strongly that a strong CO–H interaction cannot occur. On Ni and Ru, both H_2 and CO can compete more equally for surface sites thus maximizing CO–H interactions which in turn enable the restructuring of the CO adlayer. The chemisorption results obtained in this study should also shed some light on the inconsistent results reported in the literature regarding the stoichiometry of CO chemisorption on Ru. It is absolutely essential to ensure that H_2 be completely removed prior to performing CO chemisorption experiments. Trace amounts of H_2 remaining on the surface enhance CO adsorption and give inconsistent results. Because CH_4 formation was observed in the TPD studies up to 600°K, out gassing in the temperature range 575–625°K should be routinely performed prior to making chemisorption measurements.

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