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Thermal Desorption and Disproportionation of CO Adsorbed on Ru/SiO$_2$

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The dynamics of CO desorption from a Ru/SiO$_2$ catalyst have been studied by means of temperature-programmed desorption (TPD) spectroscopy and infrared spectroscopy. The adsorption of CO onto reduced Ru/SiO$_2$ leads to the appearance of tricarbonyl species and linearly adsorbed CO. The tricarbonyl species are present on Ru^{2+} cations bonded directly to the support [i.e., (SiO)$_2$Ru(CO)$_3$], whereas the linearly adsorbed CO resides on the surface of Ru crystallites. During TPD, CO is released from the tricarbonyl species at temperatures between 300 and 475 K. Desorption of linearly adsorbed CO begins at 300 K and reaches a maximum at 520 K. CO$_2$ formed via the Boudouard reaction is achieved above 500 K. No molecularly adsorbed CO is present on the catalyst surface above 675 K. CO and CO$_2$ formation at temperatures above 675 K are due to the recombination of adsorbed C and O atoms. Only linearly adsorbed CO is reactive for the formation of methane. Atomically adsorbed carbon formed by the dissociation of CO is reactive with H$_2$ in three different temperature regimes, reflecting the presence of different forms of adsorbed carbon.

INTRODUCTION

Infrared studies of CO adsorption on dispersed Ru catalysts have shown the presence of two species, linearly adsorbed CO and a multicarbonyl (*1–4*). In a recent investigation (*5*), the latter species was shown to be a tricarbonyl associated with Ru^{2+} cations bonded directly to the support [i.e., (SiO)$_2$Ru(CO)$_3$]. While studies of the strength of CO adsorption on supported Ru catalysts have been reported previously (*6–12*), these investigations have not attempted to distinguish between the different forms of adsorbed CO. Also, nothing has been said about whether CO dissociation, an important step in the hydrogenation of CO, can occur from only one or both forms of adsorbed CO. In this study, the behavior of adsorbed CO on a Ru/SiO$_2$ catalyst was examined using a combination of temperature-programmed desorption (TPD) and infrared spectroscopy. The objective of this work was to determine the relative strength of adsorption, reactivity, and interconversion of all carbon species present.

EXPERIMENTAL

The experimental apparatus used for this study has been described in Ref. (*5*). TPD-IR experiments were carried out in a small infrared cell made of stainless steel. Sapphire windows sealed to the cell permit the passage of an infrared beam through the cell. Since the window seals are limited to 723 K, TPD experiments to 873 K were performed in a quartz microreactor. Infrared spectra of the catalyst were obtained using a Digilab FTS-15/80 Fourier-transform spectrometer equipped with a narrow-band HgCdTe detector. H$_2$, CO, and He were supplied to the infrared cell or the microreactor from a gas manifold and the effluent stream was analyzed by an EAI 250B quadrupole mass spectrometer (*13*). Details concerning the sources of gases and the methods of purification are given in Ref. (*5*).

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A 3.52% Ru/SiO_2 catalyst was prepared by incipient wetness impregnation (1 m^3 solution/g support) of Cab–O–Sil HS-5 (Cabot) with an aqueous solution of $Ru(NO_3)_3$ (Engelhard). The impregnated support was dried in air at 373 K overnight. The catalyst was sieved (30–60 mesh) and 40 mg was pressed into a 1.55-cm-diameter self-supporting disk. The catalyst disk was placed in the infrared cell and then reduced in flowing hydrogen. The reduction temperature was increased at 0.2 K/s from room temperature to 673 K and then maintained at this temperature for 2 h. The sample was then outgassed for 30 min at 673 K in flowing He to remove chemisorbed hydrogen. Temperature-programmed desorption showed that H_2 completely desorbs by 420 K. A dispersion of 33% was measured by CO chemisorption following reduction in flowing H_2 at 673 K. The stoichiometry of CO to Ru was determined using the results of this study and those of Ref. (*5*). Ru weight loading was determined by X-ray fluorescence.

RESULTS

Prior to carrying out a TPD experiment, the catalyst was reduced in H_2 for 2 h at 673 K. The catalyst was then flushed with He at 673 K to remove any adsorbed H_2 and cooled to 298 K. CO was adsorbed to saturation coverage by exposing the catalyst for 15 min to a flow of He containing 50 Torr of CO at 298 K. The gas-phase CO was then flushed from the reactor and the desorption of adsorbed CO was initiated by increasing the catalyst temperature at 1 K/s. Figure 1 shows the resulting TPD spectrum. Responses for both CO and CO_2 were observed, the former being corrected for CO produced by cracking of CO_2 in the mass spectrometer. The CO spectrum is composed of a series of three overlapping peaks in the region 375 to 475 K, a broad peak centered at 520 K and a small peak centered at 775 K. The CO_2 signal becomes noticeable above 473 K and exhibits peaks at 570 and 810 K. The amount of CO_2 produced during the experiment is about 18% of the total amount of CO adsorbed. Neither H_2 nor methane was detected during the experiment.

The infrared spectra taken during ^{13}CO TPD are given in Fig. 2. The initial spectrum taken prior to the onset of desorption exhibits peaks at 2095, 2036, and 1990 cm^{-1}. The two high frequency features can be assigned to tricarbonyl species associated with highly dispersed Ru atoms, whereas the band at 1990 cm^{-1} can be assigned to linearly adsorbed CO present on the surfaces of Ru crystallites (*5*). Figure 2 shows that the CO associated with the tricarbonyl species desorbs completely by 473 K. By contrast, desorption of the linear species continues up to 673 K. No infrared features can be detected above 673 K, even though CO desorption continues to 825 K, as can be seen in Fig. 1. The frequency of the linearly adsorbed CO shifts from 1990 to 1937 cm^{-1} as desorption proceeds.

Infrared spectroscopy shows that at low CO coverages ($\theta < 0.35$) only the linearly adsorbed form of CO is present on Ru/SiO_2 (*5*). Figure 3 displays the TPD spectrum for linearly adsorbed CO. Desorption begins at 310 K and continues up to 673 K, the maximum rate of CO desorption occurring at 515 K. A CO_2 peak is also observed at 575 K. Infrared spectra obtained during the TPD experiment indicate that linearly adsorbed CO desorbs completely by 673 K.

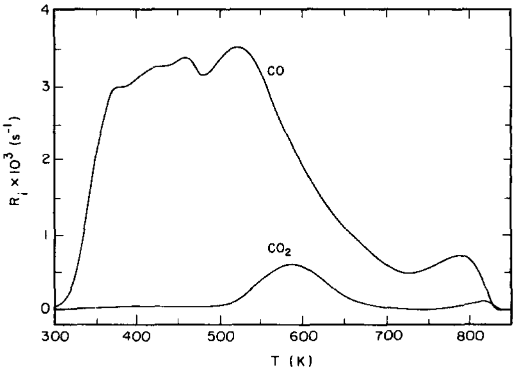

FIG. 1. TPD mass spectra of ^{13}CO adsorbed on Ru/SiO_2.

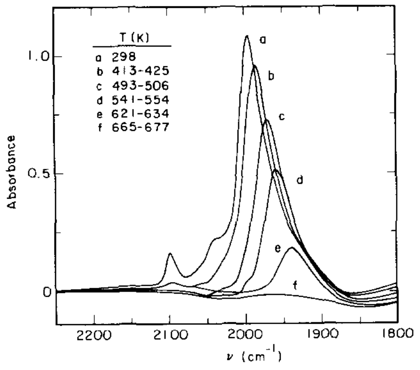

FIG. 2. TPD-IR spectra of ^{13}CO adsorbed on Ru/SiO_2.

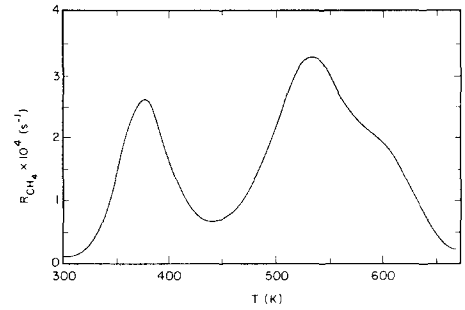

FIG. 4. TPSR mass spectra after ^{13}CO TPD to 673 K on Ru/SiO_2.

The absence of an infrared band for adsorbed CO above 673 K suggests that the CO and CO_2 evolved above this temperature during a TPD experiment are due to the recombination of adsorbed carbon and oxygen. The presence of adsorbed carbon on the catalyst surface was established as follows. A TPD experiment was carried out to 673 K and then terminated by rapidly cooling the catalyst to 298 K. A flow of H_2 was then passed over the catalyst and the temperature was raised at 1 K/s. Four micromoles per gram catalyst of methane formed as soon as the H_2 contacted the catalyst and an additional 18 μmol/g cat of methane was formed during temperature programmed surface reaction (TPSR). The TPSR spectrum, which is shown in Fig. 4, exhibits peaks at 370 and 535 K, and a shoulder at 600 K.

The recombination of adsorbed carbon and oxygen to form CO and CO_2 above 673 K was confirmed in a separate experiment. ^{13}CO was adsorbed at 298 K and then desorbed in a TPD experiment conducted up to a temperature of 673 K. The catalyst was then cooled in flowing He and ^{12}CO was adsorbed at 298 K. The TPD spectrum obtained upon desorption of ^{12}CO is shown in Fig. 5. The ^{12}CO and $^{12}CO_2$ spectra are similar to those presented in Fig. 1. What is new are the features for ^{13}CO and $^{13}CO_2$. The signal for ^{13}CO begins at 350 K and slowly rises to a broad pair of maxima located at 650 and 775 K. The signal for $^{13}CO_2$ is noticeable only above 750 K. The formation of ^{13}CO and $^{13}CO_2$ must arise from the reaction

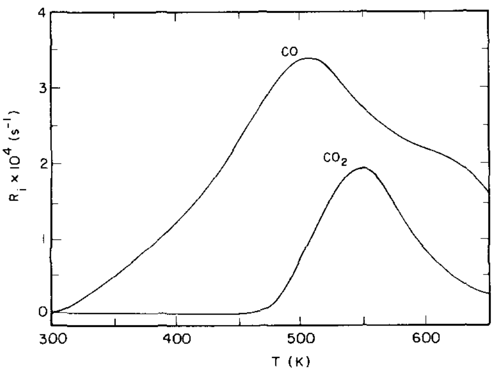

FIG. 3. TPD mass spectra of ^{13}CO adsorbed at low coverage ($\theta < 0.35$) on Ru/SiO_2.

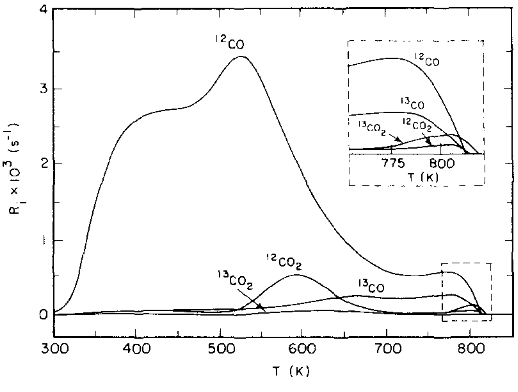

FIG. 5. TPD mass spectra after ^{13}CO TPD to 673 K followed by ^{12}CO adsorption on Ru/SiO_2.

of ^{13}C carbon and adsorbed oxygen, since all of the ^{13}CO adsorbed in the first part of the experiment was desorbed or dissociated by the time the catalyst temperature reached 673 K.

The TPSR spectrum of CO adsorbed to saturation coverage on reduced Ru/SiO_2 is shown in Fig. 6. The principal product is methane, which exhibits a single peak at 473 K. The peak for water is similar in shape to that for methane, but shifted to slightly higher temperatures. Since difficulties were experienced in obtaining reproducible calibrations for water, the signal for this product, shown in Fig. 6, cannot be used for quantitative evaluations. In addition to methane and water, a small amount of CO is observed during the low-temperature portion of the TPSR spectrum. The CO desorption peak occurs at 430 K and the total amount of CO desorbed corresponds to 10% of the CO adsorbed initially.

Infrared spectra taken during the TPSR of CO are given in Fig. 7. Between 300 and 390 K, the two high-frequency bands for CO ascribed to a tricarbonyl species decrease to zero, but the low-frequency band for linearly adsorbed CO increases noticeably. At higher temperatures, the low-frequency band shifts from 1990 cm-1 to 1937 cm-1 and decreases monotonically, completely disappearing by 570 K.

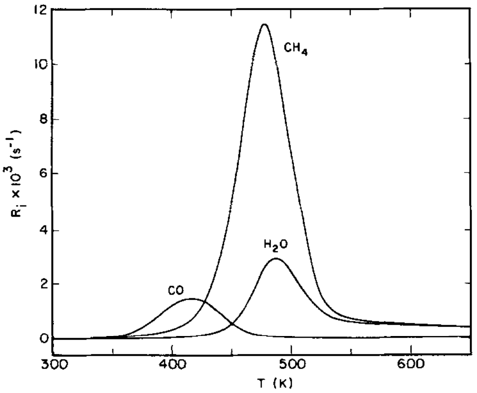

FIG. 6. TPSR mass spectra of ^{13}CO adsorbed on Ru/SiO_2.

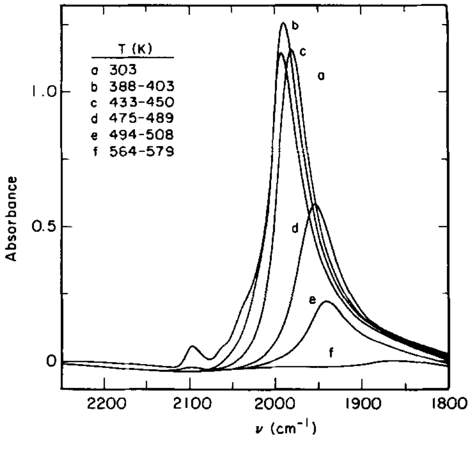

FIG. 7. TPSR-IR spectra of ^{13}CO adsorbed on Ru/SiO_2.

DISCUSSION

The number and location of CO TPD peaks observed in the TPD spectrum of adsorbed CO are in fair agreement with those observed by previous authors, as shown in Table 1. The differences in the peak temperatures may be due to differing degrees of readsorption of CO in the catalyst pores and differing heating rates (*14*). The extra CO_2 peak observed at 420 K by McClory and Gonzalez (*6*) is probably due to an oxygen impurity in the carrier gas. During the current study, when a small amount of oxygen was present in the carrier He, a CO_2 peak was observed at temperatures between 400–420 K. Comparison to Al_2O_3-supported catalysts made from $RuCl_3$ precursors is not applicable, since these catalysts retain chlorine and are not completely reduced even after hydrogen reduction at 873 K (*15–17*). Chlorine impurities and incomplete reduction strongly affect CO chemisorption, as well as the infrared and TPD spectra of adsorbed CO (*4, 11, 12*).

The TPD spectrum of CO shown in Fig. 1 can be interpreted with the aid of the results presented in Figs. 2–5. The TPD peak at 520 K can be ascribed to the desorption of linearly adsorbed CO. This assignment is

TABLE 1

CO and CO_2 Peak Temperatures during CO TPD for Ru/SiO_2

CO T(K)	CO_2 T(K)	Max. temp. recorded (K)	Ref.
— 465 650	— 515 —	773	(*7*)
— 460 650(sh)	— 547 —	723	(*8*)
— 473 643	— 553 —	723	(*9*)
405 473 698	— 540 —	750	(*10*)
373 493 723	423 573 —	723	(*6*)
410 520 775	— 570 810	873	This work

Note. sh indicates shoulder.

based on the observation that when CO is adsorbed at a coverage of less than 0.35, infrared spectroscopy shows only a single band at 1990 cm^{-1} characteristic of linearly adsorbed CO and the TPD spectrum exhibits a single peak at 515 K (see Fig. 3). The peaks in Fig. 1 located between 375 and 475 K are attributable to the Ru tricarbonyl species. As shown in Fig. 2, CO desorption from the tricarbonyl species occurs at lower temperatures than desorption from the linearly adsorbed carbonyl species. If the low-temperature portion of the TPD spectrum shown in Fig. 1 is deconvoluted using the results of Fig. 3, it is possible to sketch the full shape of the TPD spectrum associated with CO desorption from the tricarbonyl species. The integrated area for the deconvoluted spectrum of the tricarbonyl species corresponds to 18% of the CO adsorbed. This figure is in close agreement with the value of 17% obtained by selective isotopic displacement of ^{13}CO by ^{12}CO (*5*), which further supports the proposed assignment of the low-temperature CO TPD peaks observed in Fig. 1.

Above 673 K, infrared spectroscopy shows no evidence for molecularly adsorbed CO and yet the TPD spectra shown in Figs. 1 and 5 clearly show the production of CO and CO_2 above this temperature. Similar results have been reported by McClory and Gonzalez (*6*). The isotopic labeling experiment reported in Fig. 5 strongly suggests that above 673 K, CO and CO_2 are produced by the recombination of atomically adsorbed carbon and oxygen produced by CO dissociation at temperatures below 673 K. The amount of carbon liberated by CO dissociation at temperatures below 673 K is equivalent to the total amount of CO_2 produced below this temperature, 23 μmol/g cat. This figure is equivalent to the total amount of CH_4 produced during TPSR of the deposited carbon, 22 μmol/g cat. When TPD is carried out to 873 K, 14 μmol/g cat of CO and 4 μmol/g cat of CO_2 are formed in the temperature range 673 to 873 K, suggesting that 4–5 μmol/g cat of carbon remains on the surface.

The temperature at which CO dissociation becomes appreciable can be deduced from Fig. 1. As noted above, the CO_2 peak observed at 590 K is due to the reaction of CO with atomic oxygen released by the dissociation of CO. The first of these reactions is very rapid and will occur at temperatures above 420 K, if O_2 is adsorbed at room temperature. This suggests that the onset for the appearance of CO_2 is controlled by the process $CO_s \rightarrow C_s + O_s$, and not by the removal of the atomically adsorbed oxygen. From a plot of the logarithm of the rate of CO_2 desorption between 520 and 740 K vs $1/T$, an activation energy of CO dissociation of 29 kcal/mol is estimated.

The TPSR results presented in Fig. 6 show very clearly that the formation of CH_4 from adsorbed CO occurs at an appreciable rate only above 400 K. The CO produced below 400 K can be ascribed totally to desorption from tricarbonyl species. This interpretation is supported by the infrared spectra presented in Fig. 7, which shows that the two high-frequency bands of the tricarbonyl species undergo a rapid decrease in intensity with increasing reduction temperature. The small increase in intensity of the low-frequency band for linearly adsorbed CO, observed below 400 K, can be ascribed to partial readsorption of CO onto small Ru particles formed via the process $(SiO)_2Ru(CO)_3 + H_2 = 2\ SiOH +$

Ru_s-CO + 2 CO. Above 400 K, the intensity of the low-frequency band decreases monotonically, concurrent with the formation of CH_4. From these observations, we conclude that only the linearly adsorbed CO is involved with the formation of methane.

The surface carbon present on Ru/SiO_2 after CO TPD to 673 K differs in reactivity from that observed by Wise and McCarty (*18*) on Ru/Al_2O_3. In contrast to the three methane peaks observed in this study, Wise and McCarty observed only two methane peaks at 260 and 490 K. The distribution of carbon between these two peaks depended on the CO exposure time and temperature. Both peaks were assigned to isolated surface carbon atoms or clusters.

The results of this study indicate that CO molecules associated with tricarbonyl species are more weakly adsorbed than those present as linearly adsorbed CO. At the same time, isotopic displacement experiments carried out at 298 K indicate that linearly adsorbed CO readily undergoes exchange whereas CO in the tricarbonyl species does not exchange (*5*). Likewise, infrared observations show that the band for linearly adsorbed CO slowly decreases in intensity upon passage of a flow of He over a Ru/SiO_2 catalyst saturated with CO (*5*). The bands for CO adsorbed in tricarbonyl structures show no attenuation in such an experiment.

The seemingly inconsistent results of TPD and infrared experiments can be reconciled as follows. Because the tricarbonyl species occur on isolated Ru^{2+} cations (*5*), the heat of CO adsorption for such species would not be expected to vary with CO coverage. By contrast the heat of adsorption for linearly adsorbed CO on Ru particles would be expected to decrease with increasing coverage due to repulsive interactions between adjacent CO dipoles and due to the increasing competition for Ru *d* electrons needed to form Ru–C bonds. The observed shift to higher frequencies of the band for linearly adsorbed CO is a direct reflection of these effects.

CONCLUSIONS

CO adsorbed on Ru/SiO_2 is present in two forms: linearly adsorbed CO on the surface of Ru particles and tricarbonyl species associated with isolated Ru cations bonded directly to the support. The relative strength of adsorption of these two forms of adsorbed CO depends on the average CO coverage. At high coverages, linearly adsorbed CO exhibits a lower activation energy for desorption than does the tricarbonyl species, but at low coverages, the reverse relationship holds. The tricarbonyl species releases CO at temperatures between 300 and 475 K, without the formation of CO_2. The desorption of linearly adsorbed CO begins at 300 K and reaches a maximum at 520 K. CO_2 formed via the Boudouard reaction is observed above 500 K. No molecularly adsorbed CO is present on the catalyst surface above 675 K. CO and CO_2 formation at temperatures above 675 K are due to the recombination of adsorbed C and O atoms. Only linearly adsorbed CO is reactive for the formation of methane. Atomically adsorbed carbon formed by the dissociation of CO is reactive with H_2 in three different temperature regimes, reflecting the presence of different forms of adsorbed carbon.

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