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Carbon Dioxide Adsorption and Methanation on Ruthenium

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The adsorption and methanation of carbon dioxide on a ruthenium–silica catalyst were studied using temperature-programmed desorption (TPD) and temperature-programmed reaction (TPR). Carbon dioxide adsorption was found to be activated; CO_2 adsorption increased significantly as the temperature increased from 298 to 435 K. During adsorption, some of the CO_2 dissociated to carbon monoxide and oxygen; upon hydrogen exposure at room temperature, the oxygen reacted to water. Methanation of adsorbed CO and of adsorbed CO_2, using TPR in flowing hydrogen, yielded a CH_4 peak with a peak temperature of 459 K for both adsorbates, indicating that both reactions follow the same mechanism after adsorption. This peak temperature did not change with initial surface coverage of CO, indicating that methanation is first order in CO coverage. The desorption and reaction spectra for Ru/SiO_2 were similar to those previously obtained for Ni/SiO_2, but both CO_2 formation and CH_4 formation proceeded faster on Ru. Also, the details of CO desorption and the changes in CO_2 and CO desorptions with initial coverage were different on the two metals.

INTRODUCTION

Temperature-programmed desorption (TPD) and temperature-programmed reaction (TPR) were used to investigate the adsorption and methanation of carbon dioxide on a ruthenium/silica catalyst. The synthesis of methane and higher hydrocarbons from CO and H_2 (*1–16*) and the adsorption of CO (*17, 18*) on ruthenium catalysts have been studied previously, but carbon dioxide adsorption and methanation have not been studied in detail.

A recent study showed that CO_2 adsorption on nickel is activated (*19*); since nickel and ruthenium are widely used for methanation, this study was carried out to compare CO_2 adsorption and methanation on these two Group VIII metals. For comparison, carbon monoxide adsorption and methanation on Ru/SiO_2 are also presented. A silica support was used because alumina adsorbed significant amounts of CO_2 at room temperature (*20*).

EXPERIMENTAL

The experimental apparatus and procedure were described previously (*19, 21*). A 0.1-g crushed catalyst sample (60–80 mesh) was pretreated in H_2 flow at 773 K for 2 h and then cooled to room temperature in helium. Pulses (approximately 0.45 cm^3) of 10% CO in helium were injected to obtain saturation coverage at room temperature. The catalyst temperature was then increased linearly at 1.5 ± 0.1 K/s to a final temperature of 773 K in a He flow rate of 200 cm^3/min. For TPR experiments a H_2 flow rate of 250 cm^3/min was used. The desorption and reaction products were analyzed downstream continuously with a time-of-flight mass spectrometer. Quantities adsorbed and desorbed were reproducible to ± 0.4 μmole/g and the peak temperatures were reproducible to ± 3 K.

For TPD and TPR experiments, the adsorption of CO_2 was carried out at elevated temperatures. Following the same pretreatment, the catalyst was heated to the desired temperature in He, and CO_2 was pulsed over the catalyst until no additional CO_2 uptake was observed. The catalyst was then cooled to room temperature in He, and subsequently heated in He (for TPD) or in H_2 (for TPR).

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Catalyst

The procedure described by King (9) was used for the preparation of a Ru/SiO_2 catalyst. Following impregnation of $RuCl_3$ hydrate on silica (Davidson Grade 57), the sample was dried under vacuum at 373 K. The dried catalyst sample was reduced in H_2 flow at 373 K for 1 h, then at 523 K for 1 h, and finally at 623 K for 1 h. This sample was then cooled to room temperature and slowly passivated with oxygen.

A pulse flow apparatus with a thermal conductivity detector was used to measure hydrogen adsorption. At 298 K, 6.3 μmole/g of H_2 adsorbed and as the temperature was raised above room temperature, more hydrogen adsorbed. Thus, by 363 K an additional 6.8 μmole/g of H_2 adsorbed and by 438 K an additional 1.4 μmole/g of H_2 adsorbed. At higher temperatures desorption started to become significant. For the 0.8% weight loading of ruthenium, the total amount of hydrogen adsorbed at 438 K corresponds to a dispersion of 0.37. This hydrogen adsorption corresponds to a H/CO ratio of approximately unity.

RESULTS

At room temperature 27.9 μmole carbon monoxide adsorbed per gram of Ru/SiO_2 catalyst, and during heating this CO desorbed as CO (16.1 μmole/g) and CO_2 (5.9 μmole/g). As indicated in Fig. 1, CO_2 desorbed in a single peak with a peak temperature of 515 K, while CO desorbed in two peaks. The amount of desorbed CO was obtained by extending the high-temperature tail to the baseline. The silica support did not adsorb significant amounts of CO or CO_2 at room temperature or at elevated temperatures.

Only 1.7 μmole of CO_2 adsorbed at room temperature on this catalyst, and this adsorbed CO_2 desorbed as both CO_2 and CO. Carbon dioxide desorbed in two peaks with peak temperatures of 335 and 690 K; carbon monoxide desorbed in a very broad peak with a peak temperature of 750 K. Carbon dioxide adsorption increased significantly when CO_2 was adsorbed at elevated temperatures using the procedure described under the Experimental section. The maximum CO_2 adsorption was obtained at 435 K; above this temperature desorption became comparable to adsorption. As indicated in Table 1, for adsorption temperatures between 353 and 486 K, about 50% of the adsorbed carbon dioxide desorbed as CO; the rest desorbed as CO_2. Carbon dioxide desorbed in a broad peak, and the peak temperature increased from 475 to 550 K with decreasing surface coverage of CO_2, as seen in Fig. 2. Carbon monoxide also desorbed in a broad series of peaks as shown in Fig. 3. In a separate experiment following CO_2 adsorption at 435

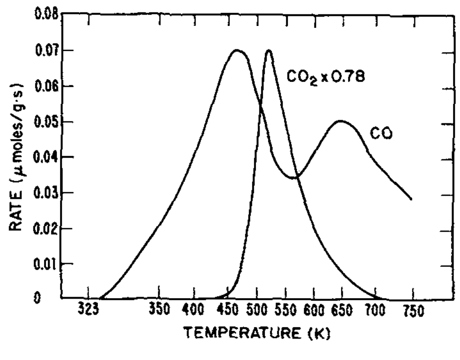

FIG. 1. Desorption spectra for carbon monoxide adsorption at room temperature.

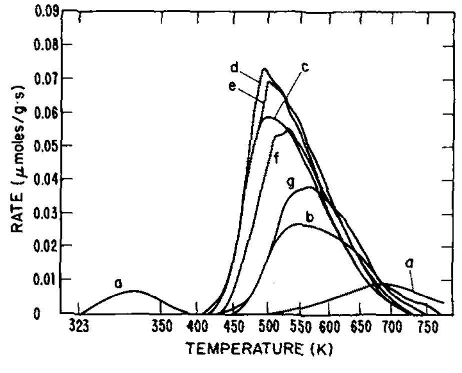

FIG. 2. Carbon dioxide spectra for carbon dioxide adsorption at (a) 298 K, (b) 353 K, (c) 388 K, (d) 408 K, (e) 438 K, (f) 453 K, and (g) 486 K.

TABLE 1

CO_2 Adsorption on Ru/SiO_2

Adsorbed gas	Adsorption temperature (K)	CO_2 adsorbed (μmole/g)	CO desorbed (μmole/g)	CO_2 desorbed (μmole/g)
CO_2	298	1.7	0.9	0.8
CO_2	353	7.0	3.3	3.7
CO_2	388	13.8	6.9	6.8
CO_2	408	14.4	7.2	7.2
CO_2	443	14.1	7.1	7.0
CO_2	453	11.8	5.8	6.0
CO_2	486	9.4	4.8	4.6
CO	298	27.9	16.1	5.9

K, the catalyst was cooled to 298 K and CO was adsorbed to saturation coverage. At 435 K the catalyst adsorbed 16.5 μmole/g CO_2 and an additional 11.2 μmole/g of CO adsorbed at 298 K. The resulting desorption spectrum was similar to that seen for CO adsorption (Fig. 1).

Methanation of carbon dioxide on Ru/SiO_2 was investigated by adsorbing CO_2 in He flow at elevated temperatures, cooling the sample to room temperature, and then switching to hydrogen carrier gas before heating. Significant amounts of H_2O were formed at room temperature when hydrogen contacted the catalyst following the adsorption of CO_2 (see Table 2). Because of the disturbance created by switching the carrier gas from He to H_2, an accurate calibration of this H_2O formed at room temperture was impossible. However, it was significantly less than the H_2O formed during subsequent heating of the catalyst in H_2 flow. Heating in hydrogen flow (TPR) following CO_2 adsorption produced both CH_4 and H_2O. Methane formed in a single peak with a peak temperature of 459 K, as shown in Fig. 4 for six adsorption temperatures. Water formed with a higher peak temperature than CH_4, and in a broad peak with a high-temperature tail. Water desorption following H_2O adsorption to saturation coverage at room temperature is also presented for comparison in Fig. 5. In these methanation experiments, all the adsorbed carbon dioxide reacted to CH_4 and H_2O, i.e., no CO or unreacted CO_2 was detected.

Figures 4 and 5 also present the methanation results for CO adsorbed at room temperature on the Ru/SiO_2 catalyst. Both CH_4 and H_2O had the same peak temperatures and peak shapes as far CO_2 methanation. About 88% of the adsorbed CO reacted to CH_4; the rest desorbed as CO with a peak temperature of 400 K; *no* CO_2 desorption was detected.

When the CO_2 adsorption temperature was increased to 523 K, 0.5 μmole/g CH_4 was formed at room temperature when He flow was switched to H_2 flow; *no* H_2O desorption was detected. Upon heating, 3.5 μmole/g CH_4 and 11.1 μmole/g H_2O

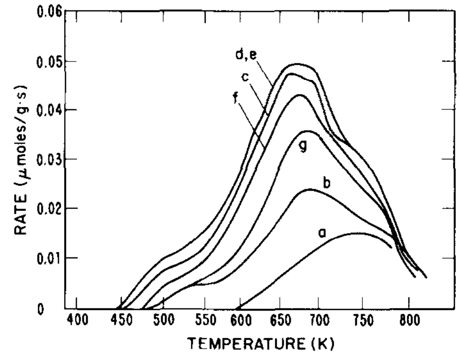

FIG. 3. Carbon monoxide spectra for carbon dioxide adsorption at (a) 298 K, (b) 353 K, (c) 388 K, (d) 408 K, (e) 438 K, (f) 453 K, and (g) 486 K.

TABLE 2

CO_2 Reaction Studies on Ru/SiO_2

Adsorbed gas	Adsorption temperature (K)	Amount adsorbed (μmole/g)	CH_4 formed (μmole/g)	H_2O formed (μmole/g)	
				(a)[a]	(b)[a]
CO_2	298	1.9	1.9	0.0	3.5
CO_2	358	7.1	7.0	2.5	7.7
CO_2	383	10.8	10.6	3.1	17
CO_2	408	14.4	14.6	2.6	19
CO_2	435	16.5	16.4	6.0	20
CO_2	448	13.8	13.7	5.4	16
CO	298	25.4	22.4	0.0	16

[a] (a) Water formed at room temperature when the carrier gas was switched from He to H_2 following CO_2 adsorption. (b) Water formed during TPR.

formed in two very broad peaks with peak temperatures of 360 and 540 K. Very similar CH_4 results were also obtained following CO adsorption at 523 K; but in the final heating 5.0 μmole/g H_2O desorbed.

Interrupted desorption experiments were also carried out following CO saturation at 298 K. The catalyst was heated above 298 K to desorb CO; at sufficiently high temperatures some CO_2 also desorbed. The catalyst was then cooled to 298 K and a normal programmed heating to 773 K was done. The CO_2 peak temperature (515 K) did not change as the CO coverage was changed by the initial heating, but the CO peak temperature increased from 486 to 602 K as the fractional CO surface coverage decreased from 1.0 to 0.46. As some CO was desorbed in the initial heating, the amount of CO desorbed during the subse-

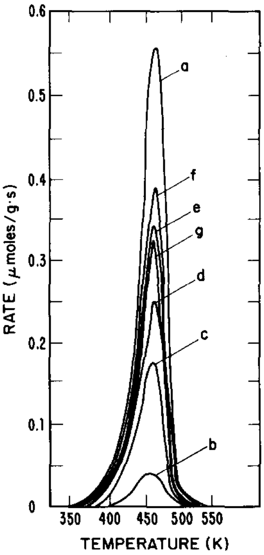

FIG. 4. Methane spectra for (a) CO adsorption at room temperature, and for CO_2 adsorption at (b) 298 K, (c) 358 K, (d) 383 K, (e) 408 K, (f) 435 K, and (g) 448 K.

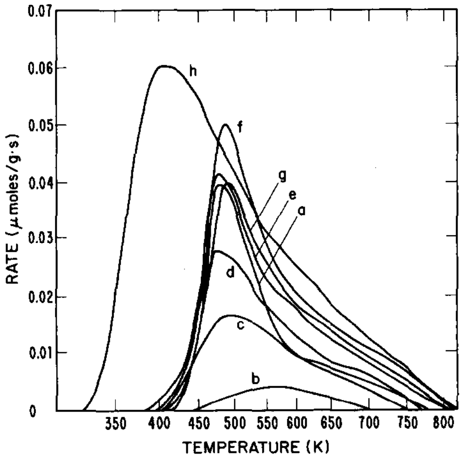

FIG. 5. Water spectra from TPR experiments for (a) CO adsorption at room temperature, and for CO_2 adsorption at (b) 298 K, (c) 358 K, (d) 383 K, (e) 408 K, (f) 435 K, (g) 448 K, and from a TPD experiment for (h) H_2O adsorption at room temperature.

quent heating decreased, but the amount of CO_2 actually increased. Detailed results are presented in Table 3. The initial heating for interrupted desorptions never exceeded 460 K.

Interrupted desorption and reaction experiments were also carried out for methanation. Following CO adsorption to saturation on ruthenium/silica, some CO was desorbed by heating in helium; the catalyst sample was cooled to room temperature and then heated in hydrogen. Methane formed in a single peak with a peak temperature of 459 K. That is, the results were the same as the lower-coverage results obtained by CO_2 adsorption. The initial heating in these experiments was also carried out in H_2 and the same results were obtained.

DISCUSSION

The increase in carbon dioxide adsorption with increasing temperature indicates that CO_2 adsorption on supported ruthenium is activated. Since silica does not adsorb significant amounts of CO_2, it is reasonable to conclude that this activated adsorption occurs on ruthenium metal, not on the support. Unlike nickel (*19*), ruthenium did not adsorb more CO_2 at room temperature when exposed to oxygen. Thus, CO_2 adsorption apparently is not sensitive to surface oxygen on Ru/SiO_2.

The similar desorption spectra obtained for CO adsorption at room temperature and CO_2 adsorption at elevated temperatures indicate that CO_2 dissociates to carbon monoxide and oxygen upon adsorption. The formation of water upon exposure to hydrogen at room temperature confirms the presence of oxygen atoms or oxygen molecules on the surface of the catalyst following CO_2 adsorption at elevated temperatures. However, the water formed at room temperature was significantly less than one H_2O for every adsorbed CO_2 (see Table 2), though the amount of water formed could not be accurately measured.

TABLE 3

Interrupted-Desorption Results on Ru/SiO_2

Amount of CO remaining after initial desorption (μmole/g)	Amount of CO desorption in the final desorption (μmole/g)	Amount of CO_2 desorption in the final desorption (μmole/g)
27.9	16.1	5.9
26.8	13.9	6.0
26.0	12.6	6.2
25.7	11.8	7.2
23.7	8.2	7.1
12.8	5.0	3.8

The reaction between oxygen and hydrogen on ruthenium has been reported to have a significant rate at 373 K (*22*) and at 298 K (*23*), so it is unlikely that the smaller formation of water at room temperature is due to a slow reaction rate of hydrogen with oxygen. The water may readsorb on the catalyst, causing only some water to be observed at 298 K. The similar spectra for water from TPR experiments and water from water adsorption suggests this possibility. However, King (*9*) reported that in the temperature range 273–500 K the rate of water desorption from Ru/SiO_2 was fast relative to the rate of water production from reaction. It is also possible that not all the adsorbed CO_2 is dissociated at room temperature, thus resulting in fewer oxygen atoms available for reaction.

Similar TPR results were obtained for both CO and CO_2 methanation (see Figs. 4 and 5) indicating that both reactions follow the same reaction path. This strongly indicates that, upon adsorption, carbon dioxide is reduced to carbon monoxide before reacting to methane. However, CO_2 is *not* reduced to carbon and two oxygen atoms (or one oxygen molecule) upon adsorption at temperatures up to 448 K.

Low and Bell (*12*) reported that carbon formed through dissociation of CO when CO was adsorbed at 523 K and above on Ru/Al_2O_3 and this carbon reacted to yield CH_4 at room temperature. For the data reported in Table 2, no methane was observed at room temperature. However, when we increased the CO_2 adsorption temperature to 523 K, methane was formed at room temperature; the same result was observed for CO adsorption at 523 K. Thus, at sufficiently high temperatures CO_2 dissociates completely on Ru/SiO_2, and the resulting carbon rapidly reacts to methane. This agrees very well with Low and Bell's results (*12*) on Ru/Al_2O_3.

The activated adsorption of CO_2 on Ru/SiO_2 catalyst enabled us essentially to carry out an initial surface-coverage variation experiment for carbon monoxide. The CO coverage varied by a factor of 12 in these experiments. The constant peak temperature obtained for CH_4 (see Fig. 4) for various initial CO coverages shows methanation is first order in CO coverage. The interrupted-desorption and interrupted-reaction experiments for CO adsorption also yielded the same methane peaks with no change in peak temperatures, further confirming the first-order dependence of methanation on CO coverage under our experimental conditions of low CO pressures and excess hydrogen.

Also, the methane peaks observed all have the same half-width—another requirement for a first-order curve. The application of the method of desorption rate isotherms (*25*) to the curves in Fig. 4 yielded a reaction order of 0.97 and an activation energy of 82.7 ± 5 kJ/mole. This corresponds to a preexponential factor of $3.6 \times 10^8\ s^{-1}$. Vannice reported activation energies of 90.4 and 91.7 kJ/mole on 1 and 5% Ru/SiO_2 (*7*).

The first-order dependence of methanation on CO coverage is consistent with CO bond breaking as the rate-limiting step for methanation in excess hydrogen. For a large H_2-to-CO ratio Randhava *et al.* (*24*) reported steady-state methanation was first-order in CO. For a H_2-to-CO ratio of 3 to 1, negative orders of reaction for CO have been observed (*2, 6*).

However, unlike the results on Ni/SiO_2 (*19*), the water peaks were not identical to the methane peaks, but were delayed to higher temperatures. If water formation was limited by water desorption from Ru/SiO_2, as indicated by Fig. 5, then our results would still be consistent with water and methane being formed at the same time, as observed on Ni/SiO_2.

Karn *et al.* (*26*) reported that on a 0.5% Ru/Al_2O_3 catalyst, the methanation of CO_2 yielded higher selectivity toward CH_4 than CO methanation. As suggested for nickel catalysts (*19, 27, 28*), the activated adsorption of CO_2 can cause a high H_2-to-CO ratio on the surface; such a high ratio favors CH_4 over higher hydrocarbons.

Both CO and CO_2 peak temperatures increased with decreasing CO coverage (see Figs. 2 and 3); this was observed for CO_2 adsorption at elevated temperatures and also for CO-interrupted desorption experiments. This shift in peak temperatures can be caused by (1) a first-order reaction with a coverage-dependent activation energy, (2) a higher-order reaction, or (3) a nonhomogeneous surface. In a TPD study of CO on clean Ru(110), Goodman *et al.* (*29*) found that the CO binding energy decreased with increasing CO surface coverage; repulsive interactions in the adlayer at higher CO coverage or a second, unresolved binding mode were suggested for decreasing CO binding energy. Identical results were also obtained for Ru(001) (*30*) and Ru(101) (*31*).

On Ni/SiO_2, no such shift in peak temperature was observed for CO_2 or CO that resulted from CO_2 adsorption (*19*). There seems to be a substantial difference in the detailed interactions of Ni and Ru catalysts with adsorbed CO and CO_2.

It is also interesting to note that following CO adsorption on Ni/SiO_2, significant CO desorption was observed at 800 K and above, while following CO adsorption on Ru/SiO_2 almost all the CO was desorbed by 800 K. In spite of this large difference in the amount of CO desorbing at high temperatures, the peak temperatures for CH_4 formation on these two catalysts differ by only

14 K and the peak shapes are almost identical.

For carbon monoxide adsorption at room temperature, the carbon dioxide peak temperature of 515 K on ruthenium was lower than the value of 556 K found on nickel (*19*). This indicates that one of the following reactions or a combination of them proceeds faster on Ru than on Ni:

$$CO_{(a)} \rightarrow C_{(a)} + O_{(a)},$$
$$CO_{(a)} + O_{(a)} \rightarrow CO_{2(g)},$$
$$CO_{2(a)} \rightarrow CO_{2(g)}.$$

Low and Bell (*12*) reported that for CO adsorption on Ru/Al_2O_3 at room temperature, CO_2 desorbed in two broad peaks with peak temperatures of 530 and 670 K, as opposed to the one sharp peak at 515 K we observed on Ru/SiO_2 (see Fig. 1). For the same experiment, CO desorbed in two peaks with peak temperatures of 480 and 620 K on Ru/Al_2O_3 catalyst (*12*). We observed similar CO peak temperatures of 450 and 640 K on Ru/SiO_2.

Also, a comparison of methane peaks from Ru/SiO_2 and Ni/SiO_2 (459 K on Ru; 473 K on Ni) (*19*) shows that methane forms at a faster rate on Ru than on Ni. This is in agreement with Vannice's steady-state experiments (*6*). The values of 400 K (*12*) and 470 K (*18*) were reported for CH_4 peaks for CO adsorption at room temperature on 5% Ru/Al_2O_3 catalyst in two previous TPR studies. A heating rate of 1 K/s was used in both of these studies. Fujimoto *et al.* (*32*), using very slow heating, reported a CH_4 peak temperature of 470 K for Ru/SiO_2 and 420 K for Ru/Al_2O_3. Both these catalysts had dispersions of 25%. Also, they observed CH_4 up to 700 K in Ru/SiO_2, while all the CH_4 was formed by 525 K in our experiments.

We observed the opposite trend with a change in support, with a peak temperature of 487 K for CH_4 from CO hydrogenation on 1% Ru/Al_2O_3 (*20*). This indicates methanation proceeds faster on our silica-supported ruthenium than on alumina-supported ruthenium. These different results obtained for methanation on ruthenium catalysts might be caused by structure sensitivity, as observed earlier by King (*9*).

A comparison of the CO_2 peaks from CO adsorption on Ni/SiO_2 and Ru/SiO_2 also indicates that CO_2 forms at a faster rate on the Ru/SiO_2 than on the Ni/SiO_2 (515 K for Ru/SiO_2 vs 556 K for Ni/SiO_2), the same trend seen for CH_4. Also, in both cases the CH_4 peak is at a lower temperature than the CO_2 peak.

If CO bond breaking is the slow step for methanation under our experimental conditions, then once the bond breaks, methane should immediately form. However, for both Ru/SiO_2 and for Ni/SiO_2 the peak temperature for CH_4 is significantly lower than the peak temperature for CO_2 formation from CO. For CO_2 to form following CO adsorption, the CO bond must first break. If CO_2 formation is limited by $CO_{(a)}$ and $O_{(a)}$ recombination or by CO_2 desorption, then this is reasonable. It is also possible that during TPR experiments, the rate of CO bond breaking is increased significantly by the presence of H_2.

CONCLUSIONS

The TPD and TPR experiments on Ru/SiO_2 indicate:

(1) Carbon dioxide adsorption on ruthenium is activated.

(2) Some CO_2, upon adsorption, dissociates into CO and O.

(3) Carbon dioxide methanation on Ru proceeds by reduction of CO_2 to CO.

(4) Methanation is first order in CO surface coverage under our conditions of low CO partial pressure and excess H_2.

(5) Carbon dioxide formation (in TPD) and methane formation (in TPR) proceed faster on Ru than on Ni.

(6) CO_2 adsorption on Ru/SiO_2 is not sensitive to O_2 exposure.

(7) Nickel and ruthenium exhibit similar behavior for CO_2 adsorption and reaction. The details of adsorption, however, are different on the two metals.

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