

## Adsorption and Methanation of Carbon Dioxide on a Nickel/Silica Catalyst

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The adsorption and methanation of carbon dioxide on a nickel/silica catalyst were studied using temperature-programmed desorption and temperature-programmed reaction. Carbon dioxide adsorption on nickel was found to be activated; almost no adsorption occurred at room temperature, but large coverages were obtained between 383 and 473 K. The data indicate CO<sub>2</sub> dissociates upon adsorption at elevated temperatures to yield carbon monoxide and oxygen atoms. These oxygen atoms react with hydrogen at room temperature, so the methane and water peaks observed during programmed heating in flowing hydrogen are identical for adsorbed CO and adsorbed CO<sub>2</sub>. Single CH<sub>4</sub> and H<sub>2</sub>O peaks, each with a peak temperature of 473 K, were observed. This peak temperature did not change with initial coverage, indicating methanation is first order in CO surface coverage. The activated adsorption of CO<sub>2</sub> allowed these coverage variation experiments to be carried out. Thus, following adsorption, CO and CO<sub>2</sub> methanation proceed by the same mechanism. However, the activated adsorption of CO<sub>2</sub> may create a higher H<sub>2</sub>:CO surface ratio during steady-state hydrogenation, causing CO<sub>2</sub> hydrogenation to favor methane over higher hydrocarbons.

### INTRODUCTION

The adsorption and methanation of carbon dioxide were studied on a nickel/silica catalyst using the techniques of temperature-programmed desorption (TPD) and temperature-programmed reaction (TPR). This study was carried out since carbon dioxide methanation has exhibited properties which indicate it may be different from carbon monoxide methanation. In particular, for CO<sub>2</sub> methanation on nickel:

- No higher hydrocarbons are observed (1-3).
- The reaction is poisoned by very low CO concentrations (1-5).
- The reaction rate is different from CO methanation (1, 2, 6).

It has been proposed that CO<sub>2</sub> first forms CO on the surface, which then reacts with hydrogen to form methane (1, 2, 6, 7).

We used TPD and TPR in an attempt to

understand these differences between the reactions since these techniques have been shown useful for CO methanation (8, 9). A nickel/silica catalyst was used instead of a nickel/alumina catalyst because alumina readily adsorbs CO<sub>2</sub>, and this makes determination of the amount of CO<sub>2</sub> adsorption on nickel difficult (10). For comparison, carbon monoxide adsorption and methanation on nickel/silica are also presented.

### EXPERIMENTAL

Temperature - programmed - desorption and temperature-programmed-reaction experiments were carried out at atmospheric pressure using the previously described flow apparatus (8). The apparatus was modified by the addition of a pulse valve which injected 0.45-cm<sup>3</sup> pulses of adsorbing gas over the catalyst surface. The pulses were either pure CO<sub>2</sub> (or CO) or 10% CO<sub>2</sub> (or CO) in helium. The diluted gases required more pulses to obtain saturation coverage, so a more accurate measure of the amount adsorbed was obtained.

The procedure for a TPD experiment

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with carbon monoxide is as follows: A 0.1-g crushed catalyst sample (60–80 mesh) was placed in a small quartz reactor, pretreated for 2 h in  $H_2$  at 773 K, and then cooled in helium. Carbon monoxide was adsorbed at room temperature by injecting pulses of CO into the helium stream until no additional adsorption was detected. The catalyst temperature was then increased linearly at  $1.5 \pm 0.1$  K/s to a final temperature of 773 K using a temperature programmer, and the temperature was measured by a small thermocouple immersed in the catalyst particles. Immediately downstream of the reactor, a time-of-flight mass spectrometer was used to continuously analyze the composition of the effluent stream from the reactor. For TPR experiments, the helium stream was replaced by hydrogen before heating the catalyst.

For TPD and TPR experiments with carbon dioxide, adsorptions were also carried out at elevated temperatures. In these experiments, following the pretreatment in  $H_2$  at 773 K and cooling to room temperature in He, the catalyst was heated to the desired temperature in flowing He, and pulses of  $CO_2$  were injected over the catalyst. The  $CO_2$  pulses were continued until no additional adsorption was detected. The catalyst was then held at the elevated temperature for approximately 90 s after the last pulse, until the  $CO_2$  background signal was almost constant. The catalyst was cooled to room temperature, held there for an additional 90 s, and then heated in He (TPD) or  $H_2$  (TPR) to 773 K.

### Catalyst

The procedure described by Bartholomew and Farrauto (11) was used for wet impregnation of nickel nitrate on silica gel (Davison grade 57). In this procedure after drying, the impregnated nickel nitrate is reduced directly in hydrogen and the resulting catalyst passivated with oxygen. The metal surface area was measured with  $H_2$  adsorption using a pulse-flow apparatus employing a thermal conductivity detector

(12, 13). Metal weight loading was measured by a gravimetric technique and by atomic absorption. The nickel/silica catalyst used in this study had a nickel weight loading of 6.9% and adsorbed  $49.0 \mu\text{mole}$  of  $H_2/\text{g}$  catalyst. This corresponds to a percentage metal exposed of 8.3% assuming an H/Ni ratio of one.

### RESULTS

The Davison silica was exposed to CO and to  $CO_2$  at room temperature following 2-hr pretreatment in hydrogen at 773 K. No CO adsorption was detected, and only  $0.2 \mu\text{mole}/\text{g}$  of  $CO_2$  adsorbed.

On the nickel/silica catalyst, only  $0.5 \mu\text{mole}/\text{g}$  of carbon dioxide adsorbed at room temperature. This  $CO_2$  desorbed by 400 K without decomposition. In contrast,  $79.7 \mu\text{mole}/\text{g}$  of carbon monoxide adsorbed at room temperature and desorbed as both CO ( $44.8 \mu\text{mole}/\text{g}$ ) and  $CO_2$  ( $16.6 \mu\text{mole}/\text{g}$ ). As indicated in Fig. 1, the  $CO_2$  desorbed in a single peak with a peak temperature of 543 K, whereas CO desorbed in three distinct peaks, with desorption continuing to high temperatures.

When the catalyst was exposed to  $CO_2$  at elevated temperatures using the procedure described in the experimental section,  $CO_2$  adsorption increased significantly, with

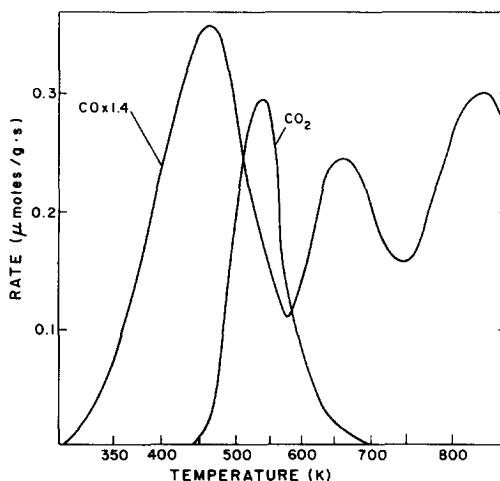


FIG. 1. Desorption spectra for carbon monoxide adsorption at room temperature.

maximum adsorption obtained near 473 K. Above 473 K, the rate of desorption became comparable to the rate of adsorption.

The adsorbed  $\text{CO}_2$  desorbed as both  $\text{CO}_2$  and  $\text{CO}$ . Table 1 indicates the amount desorbing as  $\text{CO}_2$  for each adsorption temperature; the rest desorbed as  $\text{CO}$ . For adsorption temperatures between 383 and 473 K,  $\text{CO}_2$  desorbed in a broad peak with a peak temperature of 543 K, while  $\text{CO}$  desorbed in several peaks, as indicated in Figs. 2 and 3. The correction for mass spectrometer cracking of  $\text{CO}_2$  makes the shape of the initial part of the  $\text{CO}$  curves less accurate.

Adsorption and desorption of  $\text{CO}_2$  appeared to cause a slight decrease in the amount of  $\text{CO}_2$  that subsequently adsorbed. The data in Table 1 were taken in the order listed, starting at room temperature. Thus, the amount of  $\text{CO}_2$  a fresh catalyst can adsorb at the higher temperatures is slightly higher than the values in Table 1.

The methanation of adsorbed carbon dioxide was studied by adsorbing  $\text{CO}_2$  in helium at elevated temperatures, cooling the catalyst to room temperature, and then switching to hydrogen flow before heating. When hydrogen contacted the catalyst at room temperature, water was formed in a quantity approximately equal to the amount of  $\text{CO}_2$  adsorbed. Because calibrations are a function of the carrier gas and because of the perturbation created by the switch from He to  $\text{H}_2$ , an accurate calibration of the

TABLE 1  
 $\text{CO}_2$  Adsorption on 6.9% Ni/SiO<sub>2</sub><sup>a</sup>

Adsorption temperature (K)	$\text{CO}_2$ adsorbed ( $\mu\text{mole/g cat.}$ )	$\text{CO}_2$ desorbed ( $\mu\text{mole/g cat.}$ )
298	0.5	0.5
383	14.6	6.3
398	21.6	11.6
435	31.6	16.6
443	31.6	13.8
473	28.2	9.1
523	18.3	4.0

<sup>a</sup> This catalyst adsorbs 49.0  $\mu\text{mole H}_2/\text{g}$ .

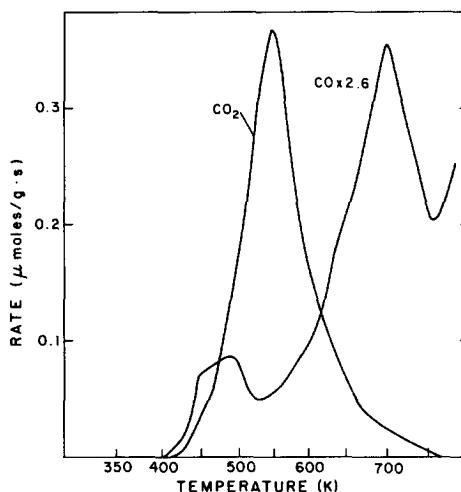


FIG. 2. Desorption spectra for carbon dioxide adsorption at 383 K.

amount of water formed as  $\text{H}_2$  was replacing He in the gas stream was impossible. During the subsequent heating in hydrogen, methane and water were formed in a single peak with a peak temperature of 473 K. Figure 4 shows the  $\text{CH}_4$  peaks for five adsorption temperatures. The  $\text{H}_2\text{O}$  peaks were essentially the same as the  $\text{CH}_4$  peaks; they had the same peak temperatures and curve shapes. The  $\text{H}_2\text{O}:\text{CH}_4$  ratio, as measured from the curve areas, was constant at unity. Almost all the adsorbed  $\text{CO}_2$  reacted to methane; for example, for 435 K adsorption, almost 98% of the adsorbed  $\text{CO}_2$  reacted to  $\text{CH}_4$  and the rest desorbed as a small  $\text{CO}$  peak at 438 K. No unreacted  $\text{CO}_2$  was detected. The amount of methane formed for the higher adsorption

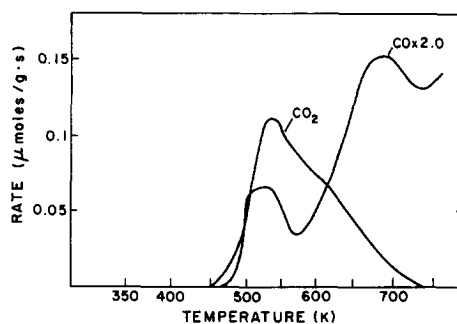


FIG. 3. Desorption spectra for carbon dioxide adsorption at 443 K.

temperatures in Fig. 4 is slightly larger than the corresponding  $\text{CO}_2$  adsorptions reported in Table 1. The difference is due to slightly higher  $\text{CO}_2$  adsorption on a freshly reduced catalyst, as mentioned.

Figure 5 shows the results of methanation of carbon monoxide adsorbed at room temperature on the nickel/silica catalyst. The  $\text{CH}_4$  and  $\text{H}_2\text{O}$  peaks are identical in peak temperature and shape to those observed for  $\text{CO}_2$  methanation, but they are larger ( $63.6 \mu\text{mole/g}$ ) due to the larger adsorption of CO. Also, a much larger unreacted CO peak was observed ( $18.8 \mu\text{mole/g}$ ), but no  $\text{CO}_2$  desorption was detected. After CO adsorption, no water formation was observed at room temperature when the helium stream was replaced by hydrogen.

#### DISCUSSION

The increase in  $\text{CO}_2$  adsorption with increased temperature indicates carbon dioxide adsorption on supported nickel is activated. Since the adsorbed carbon dioxide

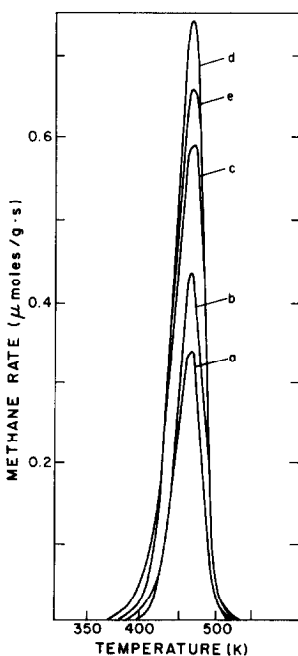


FIG. 4. Methane peaks from TPR experiments for  $\text{CO}_2$  adsorption at (a) 383 K, (b) 398 K, (c) 435 K, (d) 443 K, (e) 473 K.

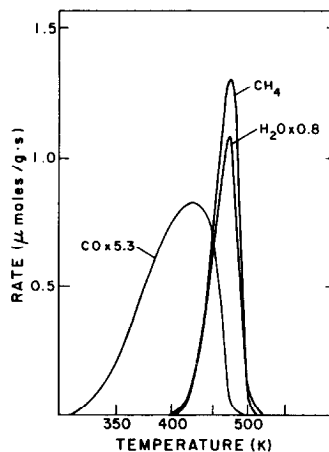


FIG. 5. Product peaks from TPR of CO adsorbed at room temperature.

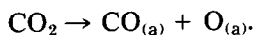
reacted almost completely to methane, and since carbon dioxide did not adsorb significantly on silica, it is reasonable to conclude that this activated adsorption occurred on the nickel metal and not the support. Other workers have also reported  $\text{CO}_2$  is very weakly bound to silica (14, 15). In our previous study (8),  $\text{CO}_2$  adsorbed at room temperature on nickel/alumina catalysts, but not on a nickel/kieselguhr catalyst. However, alumina readily adsorbs  $\text{CO}_2$  at room temperature (10), and this adsorption complicates the determination of whether any  $\text{CO}_2$  adsorbed on the nickel at room temperature.

Several studies have reported carbon dioxide absorption on nickel (15–19), and for a nickel single crystal at room temperature, the coverage was large, corresponding to 40% of the saturation CO coverage (16). In that study, when the single crystal was heated only CO was observed desorbing and Auger spectroscopy indicated oxygen remained on the surface. However, in the only study in which the amount adsorbed was measured as the adsorption temperature was varied, on unsupported nickel, activated adsorption was observed (18). We observed significant  $\text{CO}_2$  adsorption at room temperature on the Ni/ $\text{SiO}_2$  catalyst when a leak exposed the catalyst to oxygen. Also,  $\text{CO}_2$  adsorbed at room tempera-

ture on a nickel/kieselguhr catalyst which was not pretreated in hydrogen at 773 K (10). Thus CO<sub>2</sub> adsorption appears sensitive to surface oxygen.

A comparison of Figs. 1 and 2 indicates CO<sub>2</sub> desorptions from both CO and CO<sub>2</sub> adsorption are almost identical; they have the same peak temperature, 543 K, and almost the same shape. The same CO<sub>2</sub> peak was also observed for CO adsorption on a nickel/kieselguhr catalyst (8). Also similar are the high-temperature CO desorptions for CO and CO<sub>2</sub> adsorption.

The similarities between CO and CO<sub>2</sub> adsorption indicate that CO<sub>2</sub> dissociates upon adsorption at elevated temperatures:



The presence of oxygen atoms on the surface following adsorption is confirmed by the room-temperature formation of water in the presence of hydrogen. No water was observed for room-temperature hydrogen exposure following CO adsorption. At room temperature CO<sub>2</sub> is not completely dissociated into carbon and two oxygen atoms, however, since only approximately half the oxygen in the adsorbed CO<sub>2</sub> reacts at room temperature to form water. It is possible CO<sub>2</sub> completely dissociates during adsorption at the higher temperatures and carbon and oxygen recombine to form CO on cooling.

The same TPR results were obtained for both CO and CO<sub>2</sub> methanation, confirming that adsorbed CO<sub>2</sub> was dissociated into CO and O. In particular, the product peak temperatures were the same, the curve shapes were the same, and the H<sub>2</sub>O:CH<sub>4</sub> product ratio was the same (ignoring the room-temperature H<sub>2</sub>O for CO<sub>2</sub> adsorption). Because the surface coverage was larger for CO adsorption, the product peaks were larger, and because CO adsorption was at room temperature, more unreacted low-temperature CO was seen. Otherwise, the CO and CO<sub>2</sub> methanations were identical. Thus, for both adsorptions adsorbed

CO was reacting to methane, and, as proposed previously (3, 6), CO<sub>2</sub> methanation proceeds by the reduction of CO<sub>2</sub> to CO.

The activated, dissociative adsorption of CO<sub>2</sub> permitted an initial coverage variation experiment to be carried out. Thus Fig. 4 represents methanation of CO at different initial CO coverages below saturation. In TPD experiments on supported catalysts it is difficult to vary the initial coverage unless the sticking probability of the adsorbing gas is low. Otherwise, at less than saturation exposures the adsorbing gas will preferentially saturate the front part of the catalyst bed and leave the back part bare. Thus, rather than obtaining a coverage variation for different exposures of adsorbing gas, a variation of the fraction of the catalyst bed which is saturated is obtained. In the present experiments, a coverage variation was obtained since, at each adsorption temperature, the catalyst was exposed to a large excess of CO<sub>2</sub>, until no additional adsorption was detected.

Figure 4 shows that as the initial coverage of CO is varied, the peak temperature for the CH<sub>4</sub> (and also for H<sub>2</sub>O) does not change, i.e., the rate of product formation is first order in CO coverage. This is consistent with carbon monoxide bond breaking as the rate-limiting step in methanation. The rapid reaction of oxygen atoms with hydrogen and the formation of CH<sub>4</sub> and H<sub>2</sub>O at the same temperature are also consistent with this rate-determining step (8).

Our results indicate that once adsorbed, CO and CO<sub>2</sub> react at the same rate to yield methane. However, as mentioned earlier, the rates and product distributions in steady-state experiments for the two reactions are different, and CO poisons CO<sub>2</sub> methanation. The slow adsorption of CO<sub>2</sub> may be responsible for these differences. This slow adsorption could result in a higher H<sub>2</sub>:CO surface ratio than that which exists for CO adsorption, as has been previously proposed (3, 7). Excess hydrogen favors methane over higher hydrocarbons, so that CO<sub>2</sub> hydrogenates preferentially to

methane. Also, because CO adsorption is much faster than CO<sub>2</sub> adsorption, CO, even in small concentrations, will preferentially adsorb and prevent CO<sub>2</sub> methanation.

#### CONCLUSIONS

The adsorption and reaction experiments for carbon dioxide on a nickel/silica catalyst indicate that on nickel:

(1) Carbon dioxide adsorption is activated.

(2) When CO<sub>2</sub> adsorbs at elevated temperatures, it dissociates into CO and O.

(3) Carbon dioxide methanation proceeds by the reduction of CO<sub>2</sub> to CO on the surface. The activated adsorption of CO<sub>2</sub> may cause a higher H<sub>2</sub>:CO surface ratio during steady-state hydrogenation of CO<sub>2</sub>. This higher ratio would favor methane over higher hydrocarbons.

(4) Initial coverage variation experiments indicate the rate of CO methanation is first order in CO coverage.

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