

## CO Methanation on Low-Weight Loading Ni/Al<sub>2</sub>O<sub>3</sub>: Multiple Reaction Sites

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Temperature-programmed reaction (TPR) with mass spectrometric detection was used to study the hydrogenation of adsorbed carbon monoxide on low-weight loading Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. These catalysts are shown to differ from high-weight loading nickel/alumina catalysts and are shown to have two distinct pathways for carbon monoxide methanation. These pathways are attributed to two forms of adsorbed CO. The CO site which reacts at low temperature (446 K) appears to be from carbon monoxide adsorbed on nickel atoms that are bonded to other nickel atoms. It has an activation energy for methanation of 51 kJ/mol. The CO site that reacts at high temperature (546 K) has an activation energy of 145 kJ/mol. The high-temperature site, which is sensitive to the pretreatment temperature, results from CO adsorbed on nickel atoms that are interacting strongly with an oxide phase of the catalyst. Interconversion of CO between the two sites occurs and is influenced by hydrogen. Neither of the pathways appears limited by direct hydrogenation of surface carbon; this step is shown to be slightly faster under TPR conditions. The ability of TPR to measure specific reaction rates and to separate reaction pathways that might be obscured in steady-state kinetic measurements is demonstrated.

### INTRODUCTION

Temperature-programmed reaction (TPR) was used to study carbon monoxide methanation on low-weight loading Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. Previous studies have published TPR results for high-weight loading Ni/Al<sub>2</sub>O<sub>3</sub> catalysts (1, 2), but recent studies have shown that low-weight loading Ni/Al<sub>2</sub>O<sub>3</sub> catalysts behave differently (3). On Ni/SiO<sub>2</sub> (4) and on high-weight loading Ni/Al<sub>2</sub>O<sub>3</sub> (1, 2), methane forms in a distinct peak over a relatively narrow temperature range during programmed heating. However, low-weight loading Ni/Al<sub>2</sub>O<sub>3</sub> catalysts exhibit two distinct methane peaks during TPR. This paper will discuss results for a 3.2 and a 4.7% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst.

Temperature-programmed reaction has the ability to separate catalytic reaction steps in time and thus obtain information about reaction mechanisms that is unavail-

able from steady-state experiments. In particular, the presence of multiple reaction sites and parallel reaction pathways can be obscured by steady-state experiments but easily observed during programmed heating. Also, TPR measures the *specific* rates of reaction for individual sites and these rates do not depend on surface area measurements (5). The amount of reaction occurring at each site can also be measured.

For the present TPR experiments, carbon monoxide was adsorbed on a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst and the reaction products were observed during a linear temperature rise in hydrogen flow. To obtain additional information on the two distinct methane peaks, heating rate variation, interrupted reaction, and adsorptions in He and H<sub>2</sub> were done. Additional information can be obtained by varying catalyst properties and the results for TPR for a series of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts with various weight loadings will be reported (6). In the present experiments, the effect of pretreatment temperature on TPR was examined since low-weight loading Ni/

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Al<sub>2</sub>O<sub>3</sub> catalysts are not completely reduced at typical reduction temperatures (7).

#### EXPERIMENTAL

The experimental apparatus and procedure are similar to those previously described (1, 5). In a typical experiment, a 100-mg catalyst sample (60–80 mesh) rested on a quartz frit in a 1-cm-diameter quartz tube. Following pretreatment in H<sub>2</sub> (usually at 810 K for 2 h), the carrier gas was switched to helium, the sample cooled to room temperature and pulses of 10% CO in helium injected over the catalyst until saturation coverage was obtained. The carrier gas was switched back to hydrogen and the catalyst temperature was then increased at 1.0 K/s to 810 K. A constant H<sub>2</sub> flow rate of 200 cm<sup>3</sup>/min was maintained with a Tylan mass flow controller. A 0.25-mm-diameter, shielded thermocouple was located in the catalyst bed to measure temperature and provide feedback to the derivative-proportional temperature controller, which controlled the current to the electric furnace.

The gas immediately downstream of the catalyst was continuously analyzed with a UTI quadrupole mass spectrometer. A Data-General microcomputer-minicomputer system allowed simultaneous monitoring of time, temperature, and five mass peaks: methane, water, carbon monoxide, carbon dioxide, and ethane.

Several variations on the above procedure were used to obtain details of the reaction:

- Heating rate was varied.
- CO adsorption was done in hydrogen.
- Interrupted reaction experiments were carried out (4, 5).
- Pretreatment temperatures up to 1020 K were used.
- Temperature-programmed surface reaction (TPSR) (2), in which CO was exposed to the catalyst at elevated temperature in order to deposit surface carbon, was carried out.

#### Catalysts

Two low-weight loading Ni/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by impregnation of nickel nitrate on baked Kaiser A-201 alumina. The impregnated alumina was dried under vacuum at 373 K and then reduced in hydrogen according to the procedure described by Bartholomew and Farrauto (8). The final reduction temperature was 773 K; the catalyst was then passivated with oxygen in helium at room temperature. The nickel contents of the two catalysts were 3.2% (determined by atomic absorption) and 4.7% (determined by a gravimetric method (9)). The percentage reduction of the 4.7% catalyst was *estimated* with the TPD apparatus by pulsed oxygen chemisorbed at 575 K. For a pretreatment temperature of 773 K, 25% reduction was measured; the percentage did not increase significantly at higher reduction temperatures. The 3.2 and 4.7% Ni/Al<sub>2</sub>O<sub>3</sub> had approximate dispersions of 3.9 and 5.4% respectively, based on complete reduction. These dispersions were calculated from TPD of H<sub>2</sub>, which was adsorbed from flowing hydrogen as the catalyst was cooled from 773 K. This probably provides a lower limit on the dispersion, since weakly adsorbed H<sub>2</sub> is not seen. Similar TPR results were observed for both catalysts and most of the data presented will be for the 4.7% catalyst.

#### RESULTS

##### Product Spectra

In contrast to TPR results for high-weight loading Ni/Al<sub>2</sub>O<sub>3</sub> catalysts (1, 2), two distinct methane peaks were seen for nickel loadings below 11% (3, 6). Figure 1 shows the TPR spectra for the 4.7% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst which was pretreated at 773 K; carbon monoxide adsorption was done in hydrogen. For a heating rate of 1.0 K/s, the low-temperature methane (peak A) had a peak temperature of 446 ± 2 K, and the high-temperature methane (peak B) had a peak temperature of 546 ± 9 K. Peak A is rela-

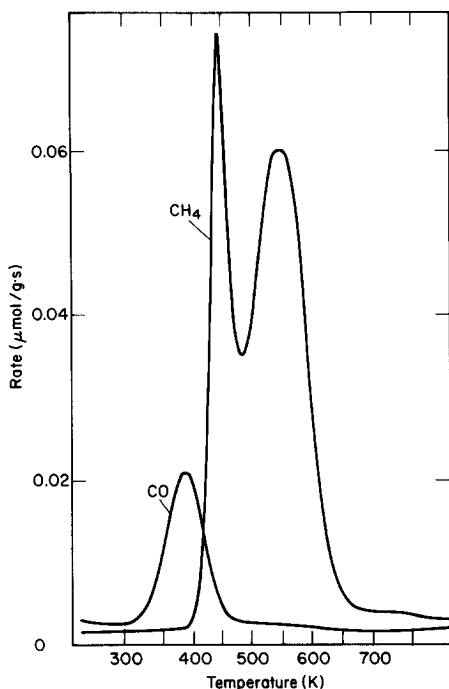


FIG. 1. TPR spectra for 4.7% Ni/Al<sub>2</sub>O<sub>3</sub>,  $\beta = 1.0$  K/s. The catalyst was pretreated at 773 K and CO was adsorbed in hydrogen.

tively narrow, while peak B is broader, and this accounts for the larger variation in peak temperatures for peak B in repeat experiments. The distinct peak structure was reproduced on three apparatus over a 2-year period.

The peak temperatures and the ratio of peak areas were the same for experiments on 100 and 30 mg of catalyst. Thus, readsorption is not causing the multiple peak structure nor is it affecting the rate of methane formation. Since methane is weakly adsorbed on nickel, readsorption should not affect the methane peaks. The separate peak areas were measured by dividing the overlapping peaks with a vertical line from the minimum point.

As shown in Fig. 1, unreacted carbon monoxide was observed at low temperatures ( $395 \pm 3$  K for 1.0 K/s heating rate); it corresponded to approximately 8% of the adsorbed CO. Water was detected in small quantities above 700 K; its appearance was

limited by readsorption on the alumina support (6). Carbon dioxide was not detected and ethane was only slightly above the noise level.

#### Kinetic Parameters

As will be shown, the peak temperatures depended on pretreatment temperature and whether adsorption was in H<sub>2</sub> or He. To study kinetic parameters, the pretreatment temperature was 810 K and adsorption was done in helium. The heating rate was varied from 0.27 to 2.1 K/s to determine activation energies without making assumptions about reaction orders or preexponential factors. With increased heating rate, peak temperatures increased, as expected. The peak temperature of peak A increased from 419 to 474 K; that of peak B increased from 588 to 624 K. However, the ratio of areas of peak A to peak B also increased, from 22:78 (A:B) at 0.27 K/s to 42:58 at 2.1 K/s (see Fig. 2). Note that the temperatures for peak B in Fig. 2 are higher than those in Fig. 1 because higher pretreatment temperature and adsorption in helium both raised the temperature of peak B.

Activation energies were determined from the slopes of two independent plots (10):  $\ln \beta/T_p^2$  versus  $1/T_p$  ( $\beta$  is the heating rate and  $T_p$  is the peak temperature) and  $\ln N_p$  versus  $1/T_p$  ( $N_p$  is the maximum desorption rate, i.e., at the peak temperature). A correction was necessary for this second plot since it requires constant coverage (10), but the ratio of peak areas depended on heating rate. Thus, instead of plotting  $\ln N_p$ , the  $\ln$  of the ratio of  $N_p$  to the amount of methane desorbed under that peak was plotted versus inverse peak temperature. Table 1 presents the activation energies obtained. The agreement between the two plots was excellent, particularly for peak A, which had an average activation energy of  $51 \pm 3$  kJ/mol. The high-temperature peak, peak B, had an average activation energy of  $145 \pm 39$  kJ/mol. The preexponential factors (A) in Table 1 were calculated from Redhead's formula (11). The uncertainties

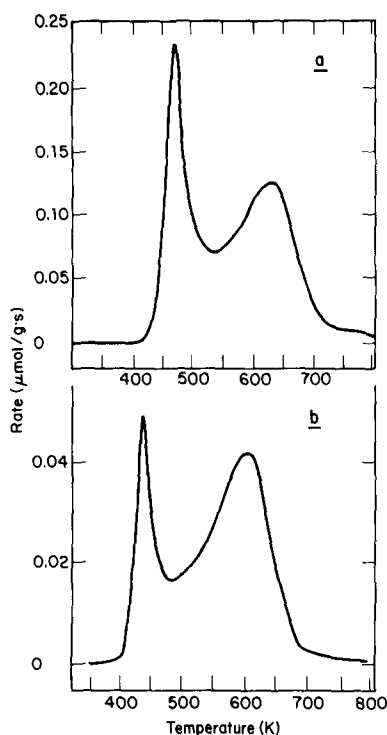


FIG. 2. Methane spectra from TPR on 4.7% Ni/Al<sub>2</sub>O<sub>3</sub> at heating rates of (a) 2.1 K/s; (b) 0.59 K/s. Carbon monoxide was adsorbed in helium and the catalyst was pretreated at 810 K.

reported both in the text and the tables are standard deviations.

The activation energies were also estimated from half-width and three-quarter width measurements (12) by assuming first-order processes. For peak A, an average value of  $53 \pm 3.5$  kJ/mol was obtained. For peak B, measurements were made after interrupted reaction and an average value of  $144 \pm 3$  kJ/mol was obtained. These values are very close to those obtained from heat-

TABLE 1  
Methane Kinetic Parameters: 4.7% Ni/Al<sub>2</sub>O<sub>3</sub>

Parameter	Peak A	Peak B
$E_a$ (kJ/mol): $\ln B/T_p^2$ vs $1/T_p$	$49 \pm 3$ (0.994) <sup>a</sup>	$144 \pm 31$ (0.939) <sup>a</sup>
$E_a$ (kJ/mol): $\ln N_p$ vs $1/T_p$	$54 \pm 3$ (0.994) <sup>a</sup>	$146 \pm 39$ (0.9016) <sup>a</sup>
$E_a$ (kJ/mol), average	$51 \pm 3$	$145 \pm 35$
$A$ (s <sup>-1</sup> )	$2.5 \times 10^4$	$2.7 \times 10^{11}$

<sup>a</sup> Linear correlation coefficient.

TABLE 2

Methanation of CO Adsorbed in He and H<sub>2</sub>

Catalyst <sup>a</sup>	Carrier gas	Peak temperature (K)		Peak area (arbitrary units)	
		A	B	A	B
3.2% Ni/Al <sub>2</sub> O <sub>3</sub>	He	446	591	$34.6 \pm 1.3$	$53.5 \pm 0.6$
3.2% Ni/Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub>	447	584	$32.8 \pm 0.6$	$71.8 \pm 0.6$
4.7% Ni/Al <sub>2</sub> O <sub>3</sub>	He	445	613	27.8	38.3
4.7% Ni/Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub>	446	592	$28.5 \pm 1.0$	$48.8 \pm 3.5$

<sup>a</sup> Pretreatment temperature, 810 K.

ing rate variation, and indicate that the assumption of a first-order process is reasonable.

#### Adsorption in Hydrogen

For both catalysts, when CO adsorption was carried out in hydrogen instead of helium, more CO adsorbed. During subsequent TPR, more unreacted CO desorbed and more methane formed in peak B. Also, the peak temperature of peak B decreased by 7 to 19 K. Peak A was unchanged for adsorption in hydrogen (see Table 2).

#### Interrupted Reaction

By partially desorbing or reacting a fraction of the adsorbed CO before a TPR was carried out, the initial coverage was varied. Several procedures were used for interrupted reaction experiments. In the first procedure, following CO adsorption in helium at 300 K, the catalyst was heated in helium to a temperature between 435 and 523 K, heating was stopped and the catalyst quickly cooled to 300 K. The carrier gas was then switched to hydrogen and a normal TPR was carried out. During the initial heating in helium for 3.2% Ni/Al<sub>2</sub>O<sub>3</sub>, the weakly bound CO desorbed, but little reactive CO desorbed. Thus, almost the same amount of methane formed for interruption in helium up to 523 K.

In each of the interrupted reactions in helium, a third peak, with a peak temperature of 750 K, appeared in the TPR methane spectra. This peak was quite small and ac-

counted for no more than 5% of the methane formed. With increased interruption temperature the percentage of methane formed under this peak increased slightly, from 3% at an interruption temperature of 435 K to 5% at 523 K.

For the second procedure, CO was adsorbed in hydrogen and the catalyst was heated in hydrogen to the interruption temperature. During this heating, methane peak A was observed. The catalyst was then cooled in hydrogen and a normal TPR was carried out. As shown in Fig. 3 for the 3.2% Ni/Al<sub>2</sub>O<sub>3</sub>, with increased interruption temperature in hydrogen, the area of peak A decreased.

A variation on this procedure was also used. After the initial heating in hydrogen to the interruption temperature (490–515

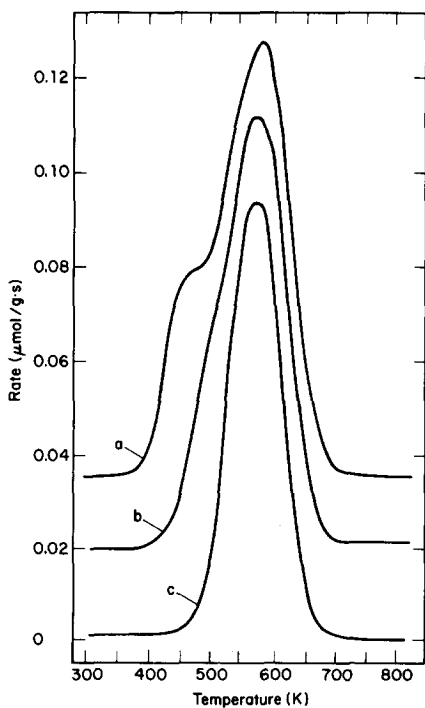


FIG. 3. Methane spectra from interrupted TPR on 3.2% Ni/Al<sub>2</sub>O<sub>3</sub>. The catalyst was initially heated in H<sub>2</sub>, heating was interrupted and the catalyst was then cooled in hydrogen before TPR. Interrupted temperatures: (a) 436 K; (b) 462 K; (c) 511 K. Carbon monoxide was adsorbed in helium. The curves are displaced vertically for clarity.

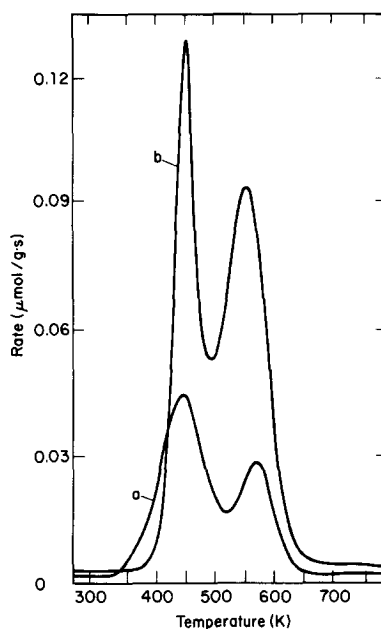


FIG. 4. Methane spectra from interrupted TPR on 4.7% Ni/Al<sub>2</sub>O<sub>3</sub>. (a) The catalyst was heated in H<sub>2</sub> to 500 K, flow was switched to He and sample was held for 10 min in He before cooling to 300 K. After an additional 10 min in He, flow was switched back to H<sub>2</sub> and a TPR carried out. Initial CO adsorption was in H<sub>2</sub> on a catalyst pretreated at 773 K. (b) Same as (a), except that additional CO exposure was given in He at 300 K before the final TPR.

K), the carrier gas was switched to helium and the catalyst held in helium for 10 min to desorb hydrogen. Separate TPD experiments for adsorbed hydrogen showed that a significant fraction of adsorbed hydrogen desorbed at these temperatures. After 10 min, the catalyst was cooled to 300 K in He and held there for 10 min before the carrier gas was switched to hydrogen. A normal TPR was then carried out. Unlike the interrupted experiments shown in Fig. 3, both methane peaks were present. As shown in Fig. 4, a somewhat broader peak A was present even though peak A was observed during the initial heating in hydrogen. Peak B was also much smaller than for a normal TPR or for an interrupted TPR. A mass balance indicated no change in total CH<sub>4</sub> yield.

This interrupted experiment was repeated, but after cooling to 300 K in He, the

catalyst was again exposed to CO pulses until saturation was reached. The subsequent TPR, shown in Fig. 4, is very similar to the normal TPR in Fig. 1. Any changes caused by the interruption in hydrogen and heating in He were apparently completely reversible.

#### Pretreatment Temperature Variation

A series of TPR experiments were carried out in which successively higher pretreatment temperatures were used. Following a 1-h pretreatment in hydrogen at 810 K and a TPR, the 4.7% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was heated for 1 h at 860 K in hydrogen. Carbon monoxide was then adsorbed in helium at 300 K and a standard TPR, up to the pretreatment temperature, was carried out. This experiment was repeated at 50 K increments to a pretreatment temperature of 1020 K.

As indicated in Fig. 5 and Table 3, the peak temperature of peak A increased

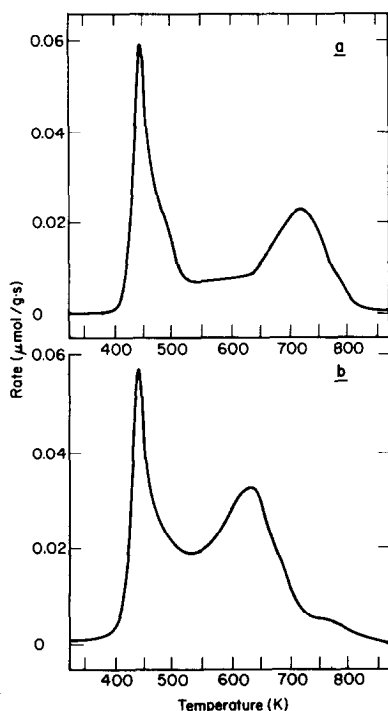


FIG. 5. Methane spectra from TPR on 4.7% Ni/Al<sub>2</sub>O<sub>3</sub>. Pretreatment temperatures: (a) 1021 K; (b) 860 K. Carbon monoxide was adsorbed in helium.

TABLE 3

Pretreatment Temperature Variations: 4.7% Ni/Al<sub>2</sub>O<sub>3</sub>

Pretreatment temperature (K)	Methane peak temperature (K)		Peak area (arbitrary units)		Peak coverage ratio A : B
	A	B	A	B	
	807	453	584	27.0	
860	446	634	33.2	47.2	0.79
914	447	676	31.4	40.5	0.78
967	451	701	31.6	41.3	0.76
1021	451	723	27.6	31.5	0.88

slightly while that of peak B increased dramatically with pretreatment temperature. With each increase in pretreatment temperature, the methane yield decreased due to the steady decrease in the amount of methane formed in peak B. The amount of methane formed in peak A went through a slight maximum with increasing pretreatment temperature. The small methane peak at 750 K was present following a pretreatment temperature of 860 K.

#### Surface Carbon Hydrogenation

Temperature-programmed surface reaction (TPSR) (2) was used to measure rates for direct hydrogenation of surface carbon. Carbon was deposited on the 4.7% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst by CO disproportionation at 573 K in helium flow (2). The catalyst was then cooled to 300 K, flow was switched to hydrogen and the catalyst was heated at 1 K/s. A broad methane peak with a peak temperature of 430–436 K was observed. A second, small methane peak was seen with a peak temperature of 580–615 K. The TPSR curves in Fig. 6 are for three carbon coverages. Note that these spectra are different from those in Fig. 1. The low-temperature methane peak is broader in TPSR and at a lower temperature. The higher temperature peak is much smaller in TPSR. The half-width measurements (12) indicated an activation energy of  $44 \pm 7$  kJ/mol for the first peak.

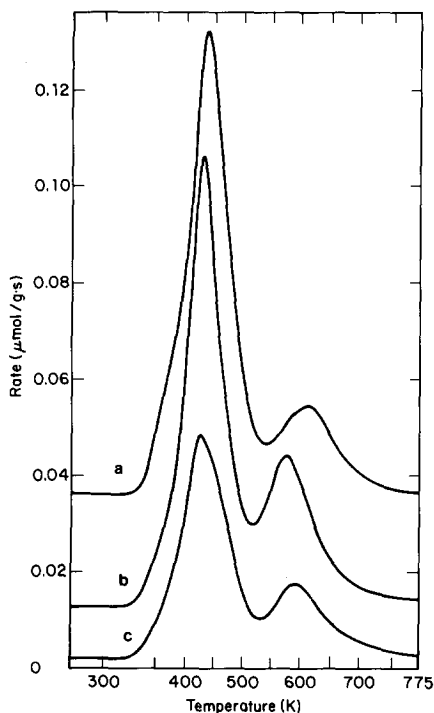


FIG. 6. Methane spectra from TPSR on 4.7% Ni/Al<sub>2</sub>O<sub>3</sub>. Carbon was deposited from CO exposure at 573 K in He. Pulses of CO (a) 2, (b) 4, (c) 6. The curves are displaced vertically for clarity.

### Carbon Monoxide Desorption

Figure 7 shows temperature-programmed desorption (in helium) of carbon monoxide which was adsorbed at 300 K in helium. The small, low-temperature CO peak has been attributed to CO from the Al<sub>2</sub>O<sub>3</sub> support (6). Carbon monoxide desorbs at high temperature from Ni/Al<sub>2</sub>O<sub>3</sub>, and a significant fraction disproportionates to CO<sub>2</sub>; CO desorption from Ni/Al<sub>2</sub>O<sub>3</sub> is quite different from CO desorption from single-crystal nickel.

### DISCUSSION

Low-weight loading Ni/Al<sub>2</sub>O<sub>3</sub> catalysts exhibit significantly different temperature-programmed reaction spectra from either Ni/SiO<sub>2</sub> (6) or high-weight loading Ni/Al<sub>2</sub>O<sub>3</sub> (1, 2, 6) catalysts. Wu and Hercules (13) also found that low-loading Ni/Al<sub>2</sub>O<sub>3</sub> catalysts exhibited XPS and ISS spectra differ-

ent from Ni/SiO<sub>2</sub>. The TPR peak temperature of the low-temperature methane peak on Ni/Al<sub>2</sub>O<sub>3</sub> is lower than the Ni/SiO<sub>2</sub> peak temperature. Fujimoto *et al.* (14) also observed, for other Group VIII metals, that the peak temperature for methane in TPR was lower on alumina-supported than silica-supported catalysts. The lower peak temperature is indicative of a higher specific activity at that temperature.

We will discuss a kinetic model for TPR on Ni/Al<sub>2</sub>O<sub>3</sub> and then discuss the type of methanation sites present.

### Reaction Mechanism

Two distinct sites for CO adsorption, designated sites A and B, are present on the nickel surface. Carbon monoxide at these sites is hydrogenated via parallel reaction pathways to methane. In addition, interconversion of CO between the sites can occur (see Fig. 8). Hydrogen appears to facilitate the conversion of CO(A) to CO(B) and

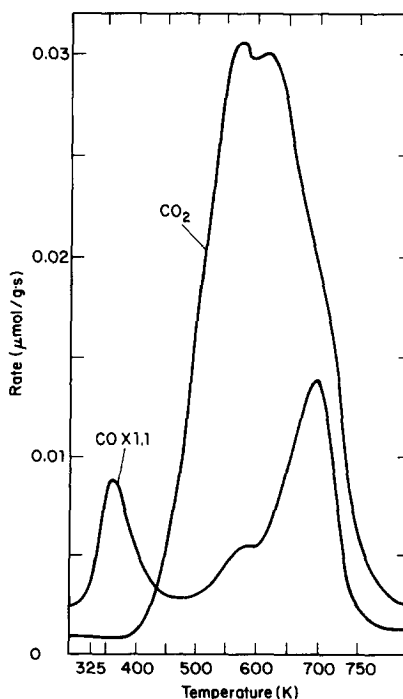


FIG. 7. TPD spectra in He following CO adsorption at 300 K on 4.7% Ni/Al<sub>2</sub>O<sub>3</sub>. The CO has been corrected for mass spectrometer cracking.

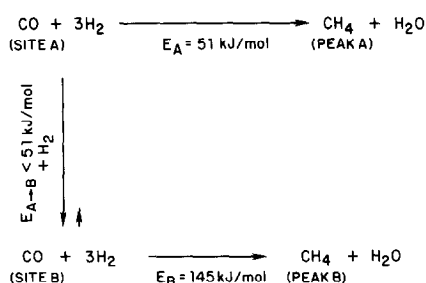


FIG. 8. Reaction scheme for CO adsorption and methanation on low-weight loading Ni/Al<sub>2</sub>O<sub>3</sub> catalysts.

to inhibit the reverse step. The activation energies for the two methanation reactions were measured by varying the heating rate, and an upper limit to the activation energy for the interconversion step was deduced. The rate of conversion of CO(B) to CO(A) is very slow under reaction conditions. The reaction of CO to methane involves carbon-oxygen bond-breaking to form an active carbon. The rate of C-O bond-breaking must be faster for CO(A) than CO(B), since the rate of methane formation does not appear to be limited by carbon hydrogenation. The next sections will explain how the data are consistent with this reaction scheme.

*The effect of heating rate.* With increased heating rate, the amount of methane in peak A increased and that in peak B decreased. This is expected if the activation energy for methanation of CO(A) is greater than that for conversion of CO(A) to CO(B). Thus, as the temperature increased, the rate of methanation of CO(A) increased faster than the rate of the conversion of CO(A) to CO(B). Since higher heating rates shift all reactions to higher temperatures (10) (see Fig. 2), higher heating rates should favor CO(A) methanation over conversion to CO(B), as observed.

*Interrupted reactions.* For interrupted reactions with initial heating in helium little reactive CO desorbed below 520 K, since the methane yield was almost unchanged. Apparently most of the CO that desorbed during this heating was from the alumina support (6, 15). Though CO did not desorb

from nickel at interruption temperatures (in He), it was able to react with hydrogen at these temperatures. The initial heating in helium did not convert CO(A) to CO(B) since the peak ratio was unchanged; apparently hydrogen is necessary for this conversion.

For interrupted reaction in which initial heating was done in hydrogen, peak A was observed during the initial heating, and during the subsequent TPR only peak B was observed. The conversion of CO(B) to CO(A) therefore is quite slow at temperatures up to 520 K, and conversion may be inhibited by hydrogen. Otherwise, CO(B) would have converted to CO(A) and then reacted rapidly to methane between 425 and 525 K. The rate of methanation of CO(A) in the subsequent TPR is thus limited by the rate of conversion of CO(B) to CO(A). This conversion may be limited by hydrogen occupation of A sites. Indeed, when hydrogen was removed from the surface by switching the carrier gas to He after interrupted heating to 500 K in H<sub>2</sub>, peak B decreased and peak A increased (Fig. 4a). Since CO(A) had already reacted completely to methane during the initial heating, the reappearance of peak A was from CO(B) that converted to CO(A). This experiment cannot be considered proof that H<sub>2</sub> inhibited the conversion of CO(B) to CO(A), however, since the 10-min holding time may have had an effect on the conversion.

*Carbon hydrogenation.* During TPR, carbon monoxide dissociates to form surface carbon, which then rapidly reacts to methane. The results for interrupted reaction in Fig. 4 and results for carbon hydrogenation indicate that methane peaks A and B are not due to hydrogenation of two forms of carbon. Peak B is from CO adsorbed in a different state than CO(A). If peak B were due to a less-active form of carbon, it would not convert to a more active form by heating in He after interrupted reaction (2) (Fig. 4a). Moreover, additional CO adsorption, after interruption in H<sub>2</sub> and heating in He,



yielded the same two methane peaks (Fig. 4b) seen in the normal TPR experiment. The same spectra would not be expected if CO was being adsorbed onto a surface that contained carbon.

Also, the peak temperatures and curve shapes for peak A are different from those obtained for carbon hydrogenation, further confirming that methane production in TPR experiments is not limited by surface carbon hydrogenation. The activation energies differ only slightly. The amount of methane in the higher-temperature CH<sub>4</sub> peak in TPSR is much smaller than that seen for peak B in TPR. Part of this higher-temperature peak in TPSR may be due to CO(B) since carbon was deposited by CO disproportionation in He at 573 K. At this temperature, CO adsorbed in the B sites may not dissociate in the absence of hydrogen. However, part of this peak may be due to hydrogenation of CO<sub>2</sub> (from the initial disproportionation of CO) which desorbs from alumina (6).

More methane was seen in peak B when adsorption was done in hydrogen instead of helium. This would not be expected if peak B were limited by carbon hydrogenation.

#### *Methanation Sites*

The two distinct methane peaks for TPR on low-weight loading Ni/Al<sub>2</sub>O<sub>3</sub> catalysts indicate the presence of two CO sites. It appears that these sites differ primarily in their degree of interaction with an oxide phase (NiO, Al<sub>2</sub>O<sub>3</sub>, or NiAl<sub>2</sub>O<sub>4</sub>). Site A is a CO adsorption site where the nickel atoms are bonded to other nickel atoms, and thus it is more prevalent on high-weight loading, extensively reduced catalysts. Site B is a CO adsorption site where the nickel atoms are bonded to nickel ions or aluminum ions in an oxide phase. Thus it is more prevalent on low-weight loading, partially reduced catalysts. The TPD results in Fig. 7 also indicate that adsorbed CO has more than one site on the surface, though disproportionation makes separation of these sites difficult.

A very small, third methane peak, which appeared only in interrupted TPR and TPR with pretreatment temperatures above 810 K, is most likely due to hydrogenation of  $\beta$ -carbon (2) formed on the surface of the catalyst.

The next sections will explain how the data are consistent with these conclusions. These distinct peaks are due to the unique interaction of alumina with nickel at low-weight loadings.

*Support effects and extent of reduction.* The support can influence both the specific activity and the number of methanation sites on nickel. Only a single methane peak was seen on Ni/SiO<sub>2</sub> (4), but multiple peaks were seen for low-weight loading Ni/Al<sub>2</sub>O<sub>3</sub> and for nickel on other supports (16). On Ni/Al<sub>2</sub>O<sub>3</sub>, as the nickel loading increased, the ratio of peak A to peak B increased significantly (6). Similarly, as the pretreatment temperature on the 4.7% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst increased, the ratio of peak A to peak B increased.

The unique TPR spectra obtained for low-weight loading Ni/Al<sub>2</sub>O<sub>3</sub> catalysts are probably due to the strong interaction of the nickel with the alumina support, which also affects the ease of reduction (7, 17–19). Wu and Hercules (13) observed significant changes in XPS spectra with weight loading of unreduced Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. In contrast, on Ni/SiO<sub>2</sub>, the location and shape of nickel XPS spectra were independent of nickel content. They concluded that nickel has little interaction with SiO<sub>2</sub>, but at low loadings nickel interacts strongly with alumina. Two types of nickel were concluded to be present on the alumina, a readily reduced nickel and a hard-to-reduce nickel (13). Others have observed that reduction of low-loading Ni/Al<sub>2</sub>O<sub>3</sub> is not complete by 810 K and the degree of reduction increases with loading and reduction temperature (7, 15, 20, 21). Wu and Hercules (13) observed that at high loadings, Ni/Al<sub>2</sub>O<sub>3</sub> was more like Ni/SiO<sub>2</sub> because of less interaction with the support. We have also observed (6) that at high loadings, Ni/Al<sub>2</sub>O<sub>3</sub> has only

one peak in TPR, as does Ni/SiO<sub>2</sub>. Burggraf *et al.* (22) also saw a significant difference between low- and high-weight loading Ni/Al<sub>2</sub>O<sub>3</sub> catalysts.

Others have reported a strong interaction between nickel and alumina. Dzis'ko *et al.* (20) noted that alumina's greater capacity to chemisorb nickel ions from impregnation solutions resulted in greater interaction between the nickel ions and the support. Zielinski (7) showed that in Ni/Al<sub>2</sub>O<sub>3</sub> catalysts of low nickel concentration (2 and 5%) most of the reduced nickel came from "fixed" nickel oxide; very little "free" nickel oxide was present. "Fixed" nickel oxide, which is most likely amorphous nickel aluminate (7, 21, 22), is much more difficult to reduce and requires temperatures up to 973 K. Reduction of amorphous nickel aluminate forms alumina in addition to small nickel crystallites, and it is quite likely that the alumina will remain in close proximity to the nickel atoms.

Infrared studies of adsorbed CO have correlated ir bands and their relative intensities with weight loading, extent of reduction, and degree of dispersion of the catalyst. For CO adsorbed on Ni/SiO<sub>2</sub> catalysts, Primet *et al.* (21) assigned a band at 2040 cm<sup>-1</sup> to CO linearly bonded to nickel atoms interacting with other nickel atoms, and a band at 2070 cm<sup>-1</sup> to CO linearly bonded to nickel atoms interacting with an oxide phase (SiO<sub>2</sub> or unreduced Ni). Carbon monoxide adsorption sites corresponding to the 2070-cm<sup>-1</sup> band were relatively more abundant on partially reduced catalysts and catalysts with smaller nickel crystallites. In studies on Ni/Al<sub>2</sub>O<sub>3</sub> catalysts, Yates and Garland (23) correlated an ir band at 2070–2110 cm<sup>-1</sup> with a CO molecule bonded linearly to nickel atoms in highly dispersed catalysts.

Infrared studies of CO adsorption bands during methanation reactions on supported catalysts have also been made (14, 24). Fujimoto *et al.* (14) observed that on 5% Ru/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> catalysts during methanation of adsorbed CO between 373 and 423

K, the broad ir band between 1960 and 1800 cm<sup>-1</sup> decreased markedly. The sharper ir band at 2020–2080 cm<sup>-1</sup> decreased slightly in this temperature region, but more markedly between 423 and 573 K. The methane TPR spectrum for the Rh/Al<sub>2</sub>O<sub>3</sub> catalyst showed two distinct methane peaks (with peak temperatures of 420 and 620 K). The methane TPR spectrum for the Ru/Al<sub>2</sub>O<sub>3</sub> catalyst also showed two peaks. Miura and Gonzalez (25) reported that on oxidized Ru, two forms of adsorbed CO are present; one form was assigned to CO on reduced Ru and the other to CO linearly adsorbed on an oxygen-perturbed Ru surface site.

These data indicate that on partially reduced, low-weight loading Ni/Al<sub>2</sub>O<sub>3</sub> catalysts, a linear form of CO, CO(B), is adsorbed on nickel atoms which directly interact with an oxide phase. CO(A) is adsorbed on nickel atoms that directly interact with other nickel atoms. Carbon monoxide(A) hydrogenates at lower temperatures and with a lower activation energy than CO(B). Thus CO that is adsorbed at A sites must hydrogenate more rapidly than CO adsorbed at B sites. The inhibition results from the interaction of the B sites with the adjacent oxide phase.

Low-weight loading and incomplete reduction increase the number of nickel atom sites interacting with an oxide phase, and thus increase the number of B sites on the catalyst. After high-temperature pretreatment, the low loading, Ni/Al<sub>2</sub>O<sub>3</sub> catalyst is still not completely reduced, and peak (B) is still present, though somewhat smaller. Higher pretreatment temperatures not only increase the number of A sites, but may also increase the interaction of some of the nickel crystallites with the oxide phase and thus increase the difficulty of hydrogenating CO(B). Therefore the methane peak from CO(B) shifts to higher temperature with higher pretreatment temperature.

*Preadsorbed hydrogen.* Preadsorption of hydrogen increased the amount of CO adsorbed and the amount of methane formed under peak B. The increased CO adsorp-

tion in the presence of hydrogen has been reported previously (26–28). The specific rate of methanation at site B increased slightly since the peak temperature decreased. Additional B sites on the catalyst surface are made available, possibly by the action of the hydrogen in forming OH groups from Ni–O units, and freeing single-atom nickel sites for bonding CO. Such sites may be more active for methanation than B sites without the adjacent OH groups. Martin *et al.* (29) reported a second state of chemisorbed hydrogen on partially reduced, supported nickel. Infrared studies of Primet and Sheppard (28) and Heal *et al.* (24) showed that preadsorbed hydrogen on Ni/SiO<sub>2</sub> catalysts produced a band at 2070 cm<sup>-1</sup> in the spectrum of adsorbed CO, a band elsewhere assigned by Primet *et al.* (21) to CO molecules linearly bonded to metallic Ni atoms interacting with an oxide phase. We also see an increase in the amount of CO bonded to such nickel atoms for CO adsorption in hydrogen.

***β*-Carbon.** *β*-Carbon was observed in two types of TPR: interrupted TPR with initial heating in helium, and a TPR following pretreatment at 860 K. The peak temperature was 750 ± 9 K. The peak temperature for peak B steadily increased with increasing pretreatment temperature from 664 K for a pretreatment temperature of 860 to 723 K for a pretreatment temperature of 1021 K. For pretreatment temperatures above 914 K, the second peak in the methane TPR spectra may consist of the two overlapping peaks, CO(B) and *β*-carbon.

Using TPSR on a 25% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, McCarty and Wise (2) observed this less-reactive form of surface carbon, designated *β*-carbon by them, with a methane peak temperature of 680 ± 30 K. In our TPSR experiments on low-weight loading Ni/Al<sub>2</sub>O<sub>3</sub>, we do not see methane formed at this temperature. The small, high-temperature peak in Fig. 6 is around 600 K and may be due to small amounts of CO(B) coadsorbed with *α*-carbon or to CO<sub>2</sub> from alumina (6).

The conditions under which *β*-carbon appeared are conditions conducive to the dissociation of some adsorbed CO (30) and subsequent diffusion of the dispersed carbon on sufficiently large nickel crystallites to form the polymerized *β*-carbon (2). Higher pretreatment temperatures may increase both the number of A sites available for CO adsorption and the number of assemblages of nickel atoms large enough to allow formation of *β*-carbon. The result in the subsequent TPR was both increased production of methane at low temperatures from CO at A sites, and increased production of methane at high temperatures from *β*-carbon.

#### CONCLUSIONS

The presence of two pathways for methanation has been observed on low-weight loading Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. These two pathways are due to hydrogenation of CO at two adsorption sites: (A) CO adsorbed on nickel atoms that are interacting with other nickel atoms; (B) CO adsorbed on nickel atoms interacting with an oxide phase of the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Temperature-programmed reaction (TPR) detected these sites because of its ability to measure specific rates of reaction. Conversion between these two sites occurs but is influenced by surface hydrogen. The alumina support increases the difficulty of reducing nickel and creates B sites on the partially reduced catalysts and on the catalysts where nickel atoms interact intimately with the oxide support.

Neither of the pathways appears to have the hydrogenation of dispersed surface carbon as a rate-limiting step, though there is some methane produced at high temperatures from the hydrogenation of polymerized *β*-carbon formed during interrupted TPR. The hydrogenation of CO(A) had an activation energy of 51 kJ/mol; the hydrogenation of CO(B) had an activation energy of 145 kJ/mol. Both pathways for the hydrogenation of CO should be present in

steady-state kinetic studies on low-weight loading Ni/Al<sub>2</sub>O<sub>3</sub> catalysts.

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#### REFERENCES

- Zagli, A. E., Falconer, J. L., and Keenan, C. A., *J. Catal.* **56**, 453 (1979).
- McCarty, J. G., and Wise, H., *J. Catal.* **57**, 406 (1979).
- Zagli, A. E., Ph.D. dissertation, University of Colorado, Department of Chemical Engineering, November, 1981.
- Falconer, J. L., and Zagli, A. E., *J. Catal.* **62**, 280 (1980).
- Falconer, J. L., and Schwarz, J. A., *Catal. Rev. Sci. Eng.* **25**, 141 (1983).
- Kester, K. B., Zagli, E., and Falconer, J. L., to be submitted for publication.
- Zielinski, J., *J. Catal.* **76**, 157 (1982).
- Bartholomew, C. H., and Farrauto, R. J., *J. Catal.* **45**, 41 (1976).
- Skoog, D. A., and West, D. M., "Analytical Chemistry. An Introduction," 2nd ed., p. 157. Holt, Rinehart & Winston, New York, 1974.
- Falconer, J. L., and Madix, R. J., *J. Catal.* **48**, 262 (1977).
- Redhead, P. A., *Vacuum* **12**, 203 (1962).
- Chan, C. M., Aris, R., and Weinberg, W. H., *Appl. Surf. Sci.* **1**, 360 (1978); Chan, C. M., and Weinberg, W. H., **1**, 377 (1978).
- Wu, M., and Hercules, D. M., *J. Phys. Chem.* **83**, 2003 (1979).
- Fujimoto, K., Kameyama, M., and Kunugi, T., *J. Catal.* **61**, 7 (1980).
- Bartholomew, C. H., and Pannell, R. B., *J. Catal.* **65**, 390 (1980).
- Ozdogan, S. Z., Gochis, P. D., and Falconer, J. L., *J. Catal.* **83**, 257 (1983).
- Shalvoy, R. B., Reucroft, P. J., and Davis, B. H., *J. Catal.* **56**, 336 (1979).
- Shalvoy, R. B., Davis, B. H., and Reucroft, P. J., *SIA, Surf. Interface Anal.* **2**, 11 (1980).
- Bartholomew, C. H., Pannell, R. B., and Butler, J. L., *J. Catal.* **65**, 335 (1980).
- Dzis'ko, V. A., Noskova, S. P., Borisova, M. S., Bolgova, V. D., and Karakchiev, L. G., *Kinet. Catal.* **15**, 667 (1975).
- Primet, M., Dalmon, J. A., and Martin, G. A., *J. Catal.* **46**, 25 (1977).
- Burggraf, L. W., Leyden, D. E., Chin, R. L., and Hercules, D. M., *J. Catal.* **78**, 360 (1982).
- Yates, J. T., Jr., and Garland, C. W., *J. Phys. Chem.* **65**, 617 (1961).
- Heal, M. J., Leisegang, E. C., and Torrington, R. G., *J. Catal.* **42**, 10 (1976).
- Miura, H., and Gonzalez, R. D., *J. Phys. Chem.* **86**, 1577 (1982).
- Horgan, A. M., and King, D. A., in "Adsorption Desorption Phenomena" (F. Ricca, Ed.), p. 329. Academic Press, New York/London, 1972.
- Van Ho, S., and Harriott, P., *J. Catal.* **64**, 272 (1980).
- Primet, M., and Sheppard, N., *J. Catal.* **41**, 258 (1976).
- Martin, G. A., Ceapalan, N., Montgolfier, P., and Imelik, B., *J. Chim. Phys.* **70**, 1422 (1973).
- Rabo, J. A., Risch, A. P., and Poutsma, J. L., *J. Catal.* **53**, 295 (1978).