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Reactions of Carbon Monoxide and Hydrogen on Co, Ni, Ru, and Pd Metals

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The adsorption of CO on Ni at 300°C is dissociative, resulting in disproportionation to CO_2 and a Ni–C species. The surface carbon species formed from CO is readily hydrogenated at 300°C to methane. At room temperature, the CO sorption on Ni is nondissociative, and the adsorbed CO is inert to H_2. In contrast, the Ni–C species formed from CO at 200 to 300°C reacts with H_2, even at room temperature, forming C_1 to C_4 paraffins. Co and Ru metals show behavior very similar to that of Ni. In contrast to Ni, Co, and Ru metals, the adsorption of CO on Pd at 300°C is nondissociative, and the chemisorbed CO is less reactive to H_2 than the M–C species formed on Ni, Co, or Ru.

INTRODUCTION

The chemistry of $CO + H_2$ reactions, including the reaction between CO and Fe, Co, or Ni metals, and between H_2 and the carbides of the same metals, have been studied by many investigators (*1–21*). A significant part of the earlier work concentrated on the chemistry and thermodynamics of crystalline bulk carbide phases (*1–14, 22, 23*), with the interest of elucidating the reaction mechanism of hydrocarbon synthesis. Since the chemistry and thermodynamics of bulk phases are different from those of surface species, the present work was aimed at the study of surface species, for example, surface carbon species, rather the bulk carbides previously described. In addition, Pd was added to the metals studied because this metal, in contrast to Co, Ni, and Ru, is noted for its very low activity in hydrocarbon synthesis. To preserve the primary surface species as much as possible and to minimize secondary reactions such as the migration of the surface carbon to the bulk, we adopted the pulse technique in this study. With this experimental technique, the time of exposure of the catalyst to reactants can be reduced to a few seconds, and the catalyst, with its freshly formed surface layer, can be quenched from the reaction temperature to any desired low temperature in a few seconds. In addition, the amount of reactant can be reduced to a monolayer, or to even smaller quantities.

The reaction of CO on Ni and the reaction of the produced Ni–C species with H_2 have been studied recently using a pulse technique similar to the one adopted here (*21*). The published data are somewhat incomplete, however, in that they deal only with Ni metal in a narrow reaction-temperature range.

EXPERIMENTAL NOTES

Apparatus and Analysis

The apparatus used in this investigation consisted of a pulse reactor system com-

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TABLE 1

Characteristics of Evaluated Catalysts[a]

Catalyst	Sample composition	Adsorbed CO (mmol/g of catalyst)	Percentage metal dispersion
A	4.9% Pd/SiO_2[b]	0.096	21.3
B	7.0% Ni/SiO_2	0.033	2.8
C	2.7% Ni/SiO_2	0.017	3.7
D	7.3% Co/SiO_2	0.028	2.3
E	7.3% Co/SiO_2[c]	0.017	1.4
F	1.2% Ru/SiO_2	0.065	54.2

[a] All tests were conducted on 1.0-g samples, except for catalyst C, which was a 1.5-g sample. The temperature was 23°C.

[b] SiO_2, silica gel; Davison Grade 57.

[c] The 7.3% Co/SiO_2 catalyst is listed twice because the metal dispersion of the D sample was lowered from 2.3 to 1.4% (Catalyst E) by a series of oxygen treatments administered during an experiment.

posed of a pulse injection valve (Carle #1101), a Pyrex U-tube reactor, a fluidized bed furnace, and a gas chromatograph (gc) equipped with a −195°C cold trap. The reactor U-tube was about 1.5 in. wide, 10 in. long, and was constructed of 10-mm-o.d. pyrex tubing. The pulse injection valve delivered ~2 cm^3 of CO or H_2 into a He carrier stream which is routed through the catalyst bed into the gc at a flow rate of approximately 50 cm^3/min and a pressure of 40 psi. The He stream (Linde ultra high purity grade) was purified by initial passage through an oxygen getter (Oxy Trap code #4003, Altech Associates) and a 500-cm^3 molecular sieve column (Linde 3A) cooled to −195°C.

The catalyst bed in the U-tube was typically a 1.0- or 1.5-g sample of metal-impregnated silica gel, ground and sieved to 10 to 20 mesh. A fresh, prereduced catalyst sample was typically treated in flowing H_2 at 250 to 500°C for 16 hr *in situ* prior to evaluation. After reduction, the catalyst was purged with He before cooling to the desired temperature of investigation.

The gas stream was analyzed with a Hewlett Packard #5750 gas chromatograph equipped with a 9 × 0.5-in. Poropak Q column. In a typical experimental sequence, a CO pulse was charged to the catalyst via the He carrier gas, and the unreacted CO was measured. The CO_2 generated by the reaction was frozen in the −195°C trap until it was analyzed by warming the trap to 100°C and introducing the gas into the gc. The procedure gave an accurate determination of adsorbed CO and adsorbed surface carbon (equivalent to CO_2 production) along with the degree of CO disproportionation. The subsequent H_2 pulse(s) was delivered to the He stream without the −195°C trap, and the produced CH_4 was analyzed. In the overall analysis procedure, CO, CH_4, and CO_2 were determined quantitatively with the gc column at room temperature. Other gas products (C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, and C_5H_{12}) were measured via programming the gc column from room temperature to 200°C at 10°C/min. The quantity of products and standards was determined with a Spectra Physics Autolab minigrator. The error in determination of quantities was estimated at ~2%, based on repeated injections and operational experience.

Catalyst Preparation and Characteristics

The metals used in this study were supported on silica gel. They were prepared by adsorbing aqueous (concentrated HCl diluted with an equal volume of water, in the case of the Pd catalyst) solutions of metal nitrates or chlorides onto Davison Grade 57 silica gel. Excess solvent was removed by drying in a rotoevaporator at 40 to 50°C. The catalysts were normally air-calcined at 300 to 400°C for 0.5 to 2 hr prior to reduction in H_2. The H_2 reduction sequence typically involved 0.5 to 2 hr in flowing H_2 at 150 to 300°C, followed by 2 hr or more at 450 to 500°C. Subsequent catalyst reduction was carried out in the pulse reactor before the adsorption study. The characteristics of the catalyst studied are given in Table 1. Each sample was analyzed for metal content, and the metal dispersion was determined by CO adsorption at room temperature by the pulse technique described above. As a matter of convenience, the amount of CO adsorbed at room temperature on 1 g of catalyst was used as a reference value and was defined as a "monolayer." The column designated Adsorbed CO is the number of millimoles of chemisorbed CO at 23°C on a 1-g catalyst sample. The value calculated as Percentage metal dispersion quantitated the fraction of metal atoms capable of interacting with CO, assuming a CO to metal atom ratio of 1:1 in the surface complex.

Data Presentation

We have reported most of the data generated in this investigation as a function of the amount of CO adsorbed at room temperature on the specific catalyst under examination.

The amount of CO adsorbed at room temperature (see Table 1) is defined as a "CO monolayer" and consequently defines the concentration of CO active surface sites on the catalyst. The quantity of each product gas is listed in the tables in units of mole percent produced per mole of CO adsorbed at 23°C or, indirectly, as percentage of product per monolayer. The reaction products from CO are typically breakthrough CO gas, adsorbed CO, effluent CO_2, and carbon deposited on the catalyst. The H_2 pulse generated mainly CH_4, along with significant levels of higher hydrocarbon homologs. The column labeled Percentage carbon distribution (Tables 11–14) itemizes the mole-percent of carbon allocation among the hydrocarbon products.

The carbon layer deposited on the catalysts consisted of an active (carbidelike) and an inactive (graphitelike) surface carbon, and probably a certain amount of bulk carbide, depending upon the concentration, temperature, and time of exposure. In this study we shall use the term "surface carbon" to indicate all carbon species present.

In the pulsing experiments, the following reaction sequences were examined with each catalyst:

1. A CO pulse was introduced over the clean catalyst surface at 300°C, followed by hydrogen at 300°C and higher temperatures.
2. A CO pulse was introduced over the clean catalyst at 300°C, followed by cooling to 23°C. Subsequently, H_2 was pulsed over the catalyst bed at various temperatures.
3. A CO pulse was adsorbed on the clean surface at room temperature, followed by H_2 pulses at various temperatures.

RESULTS

Surface Reactions of Carbon Monoxide and Hydrogen over Pd, Ni, Co, and Ru at High Temperatures

1. Study of palladium. As a standard procedure for all catalysts studied, the reduced 4.9% Pd/SiO_2 catalyst sample (Catalyst A in Table 1) was first degassed in helium flow at 300°C for 1 hr. Subsequently, a CO pulse was introduced at 300°C. As a matter of convenience, the amount of CO adsorption observed at room temperature is used as a reference value, and it is defined as "monolayer." In the following sections, X% surface layer will mean a surface layer equivalent to X% of the "monolayer." According to Table 2, the CO pulsed at 300°C produced very little disproportionation to $CO_2 + C$, as measured by the CO_2 effluent, and the retained surface coverage was about 63% of a monolayer. Based on the amount of CO retained and the CO_2 in the effluent, the surface overlayer consisted of 99% CO and 1% C. A subsequent pulse of excess H_2 converted about one-third of the chemisorbed CO to methane, and an additional six H_2 pulses converted about half of the remaining CO to methane.

A question arises as to whether the adsorbed CO consists of CO molecules or species dissociated into distinct Pd–C and Pd–O surface complexes. This problem was

TABLE 2

CO and H_2 pulses over 4.9% Pd/SiO_2 (Catalyst A)[a]

Gas pulsed	Catalyst temperature (°C)	Products (% of monolayer)	Surface layer (% of monolayer)
CO	300	27.0–CO	
		0.6–CO_2	
		0.6–C ads.	63.0
		62.4–CO ads.	
H_2	300	19.0–CH_4	44.0
H_2	300	7.9–CH_4	36.1
H_2 (five pulses)	300	17.7–CH_4	18.4

[a] Pulse size, 90.6% of a monolayer.

resolved by delivering two successive CO pulses to a fresh catalyst sample at 300°C. If the first pulse was adsorbed as C and O, then a second pulse of CO should produce CO_2 corresponding to the surface Pd–O. The data showed only a minor increase of CO_2 in the effluent of the second CO pulse, indicating that the CO adsorbed on Pd is associated. In order to verify that the Pd–O surface species is indeed reactive to CO, a clean, reduced Pd surface was exposed first to a small O_2 pulse, which resulted in a surface coverage corresponding to 88% of a monolayer. The subsequent single CO pulse converted 54.5% of the adsorbed oxygen to CO_2, verifying that adsorbed oxygen on Pd readily reacts with CO.

2. Study of Nickel. Two Ni/SiO_2 samples were studied (Catalysts B and C in Table 1). The catalyst containing 7% nickel had twice the CO monolayer capacity of the 2.7% Ni sample, indicating a finer metal dispersion on the 2.7% Ni catalyst. Both samples were pulsed at 300°C with CO, followed by a H_2 pulse. On the 7% Ni catalyst, the CO pulse produced 147% surface coverage relative to a monolayer, and the surface overlayer contained 77% C and 23% CO. The fresh 2.7% Ni sample yielded ~132% surface layer consisting of 85% C and 15% CO. As mentioned before, the term "surface carbon," or "surface layer," includes all carbon species including the bulk species. With both catalysts, the first H_2 pulse converted about 80% of the surface species to methane, as shown in Tables 3 and 4. The second hydrogen pulse on Catalyst B (7% Ni) converted 40% of the residual surface layer to methane (Table 3), while with Catalyst C (2.7% Ni) it converted only about 6% of the residual surface layer to methane (Table 4). With both catalysts, at 300°C, the unreactive surface residue after the hydrogen pulses was typically between 10 and 20% of a monolayer.

The exposure of Catalyst C to three cycles consisting of a CO pulse and two subsequent H_2 pulses at 300°C resulted in a very small decline in the reactivity of the Ni surface for CO disproportionation (Table 4). The CO_2 produced by the third cycle was only about 3% less than in the original pulse of the first cycle. A cumulative unreactive residue equal to 52% of a monolayer remained on the surface after two hydrogen pulses of the third cycle.

The surface carbon produced by a subsequent CO pulse at 300°C (Table 4) was heated at 500°C for 1 hr. Upon pulsing this heat-treated overlayer with hydrogen at 300°C, the CH_4 recovery from the treated surface was only 2% of the surface carbon, which clearly indicates changes in the chemistry of the carbon. It was found that heat treatment of the carbon over-

TABLE 3

CO and H_2 Pulses over 7.0% Ni/SiO_2 (Catalyst B)[a]

Gas pulsed	Catalyst temperature (°C)	Products (% of monolayer)	Surface layer (% of monolayer)
CO	300	3.4–CO 113–CO_2 113–C ads. 34.6–CO ads.	147
H_2	300	114–CH_4	33.0
H_2	300	13.0–CH_4	20.0
H_2 (eight pulses)	300–500	2.7–CH_4	17.3

[a] Pulse size, 264% of a monolayer.

TABLE 4

H_2 over 2.7% Ni/SiO_2 (Catalyst C)[a]

Gas pulsed	Catalyst temperature (°C)	Product (% of monolayer)	Surface layer (% of monolayer)	Cumulative surface residue (% of monolayer)
CO	300	121–CO 111–CO_2 111–C ads. 21.0–CO ads.	132	
H_2	300	111–CH_4	21.0	
H_2	300	1.3–CH_4	19.7	19.7
CO	300	128–CO 109–CO_2 109–C ads. 18.0–CO ads.	127	
H_2	300	108–CH_4	19.0	
H_2	300	1.3–CH_4	17.7	37.4
CO	300	134–CO 108–CO_2 108–C ads. 14.0–CO ads.	122	
H_2	300	106–CH_4	16.0	
H_2	300	1.3–CH_4	14.7	52.1
CO	300	139–CO 104–CO_2 104–C ads. 17.0–CO ads.	121	
Heat 1 hr	500			
H_2	300	2.6–CH_4	118	170
CO	300	189–CO 79.0–CO_2 79.0–C ads. 17.0–CO ads.	96	

[a] Pulse size, 364% of a monolayer.

TABLE 5

CO and H_2 Pulses over 2.7% Ni/SiO_2 (Catalyst C)[a]

Gas pulsed	Catalyst temperature (°C)	Product (% of monolayer)	Cumulative surface layer (% of monolayer)
CO	310	155–CO	
		100–CO_2	
		100–C ads.	113
		13.0–CO ads.	
CO	310	272–CO	
		43.0–CO_2	
		43.0–C ads.	166
		10.0–CO ads.	
CO	310	284–CO	
		34.0–CO_2	
		34.0–C ads.	216
		16.0–CO ads.	
H_2 (three pulses)		167–CH_4	49

[a] Pulse size, 368% of monolayer.

layer at 300°C for 1 hr does not produce a significant decline in the subsequent CH_4 recovery. A fifth CO pulse at 300°C over the 500°C pretreated surface carbon produced 30% less CO_2 than the fresh surface. Thus, the disproportionation of CO on nickel is affected by the presence of residual unreactive surface carbon, and it declines substantially in the presence of a dense carbon overlayer (Table 5).

3. Study of cobalt. The 7.3% Co/SiO_2 catalyst (Catalyst D in Table 1) was treated in a manner similar to the nickel catalysts. Charging with a CO pulse at 300°C resulted in 159% surface coverage consisting of 89% C and 11% CO. The first H_2 pulse converted 60% of the surface species to CH_4, somewhat less than the 80% conversion observed with Ni. Near-quantitative recovery of the surface layer, however, was achieved with several subsequent hydrogen pulses at 400 and 500°C (Table 6). Pulsing of a fresh Co surface with CO at 400°C essentially reproduced the results obtained at 300°C.

4. Study of ruthenium. Exposure of the 1.2% Ru/SiO_2 catalyst (Catalyst F in Table 1) to a CO pulse at 300°C resulted in about 40% surface coverage consisting of about 70% C and 30% CO (Table 7). The initial H_2 pulse converted about 80% of the surface species to CH_4. Pulsing a fresh Ru catalyst surface at 400°C with CO resulted in surface coverage consisting of 81% C and 19% CO, which indicates a higher degree of disproportionation at the higher temperature. Six subsequent H_2 pulses converted 88% of the surface coverage to CH_4.

The Reactivity of Surface Carbon and Chemisorbed CO at Low Temperature

Data in the literature (*21*), as well as the data presented in the previous section, show that, at 300°C over Ni, Co, and Ru metals, the surface carbon coexists with chemisorbed CO. Since our experimental data show that both species are converted at least partially by hydrogen to methane at 300°C, a distinction between the reactivity of these two species at this temperature is difficult. For this reason, the deter-

TABLE 6

CO and H_2 Pulses over 7.3% Co/SiO_2 (Catalyst D)[a]

Gas pulsed	Catalyst temperature (°C)	Products (% of monolayer)	Surface layer (% of monolayer)
CO	300	11.0–CO 142–CO_2 142–C ads. 17.0–CO ads.	159
H_2	300	97.0–CH_4	62.0
H_2	300	11.0–CH_4	51.0
H_2	300	1.6–CH_4	49.4
H_2	400	18.0–CH_4	31.4
H_2 (seven pulses)	400–500	27.3–CH_4	4.1

[a] Pulse size, 312% of a monolayer.

mination of the relative reactivities of these two species would require the examination of pure surface carbon and pure chemisorbed CO species. At higher temperatures, the amount of chemisorbed CO in the surface layer can be reduced, and a surface coverage consisting mainly of carbon can be attained. At temperatures above 300°C, however, the primary surface carbon species degrades into a less-reactive form. For this reason, the comparison between surface carbon and chemisorbed CO was carried out at low temperatures. Since preliminary experiments indicated that CO disproportionation is first observed at approximately 150°C, our study of the carbon overlayer was carried out between room temperature and approximately 200°C.

1. Study of palladium. With palladium (Catalyst A), the disproportionation of CO and the corresponding surface carbon formation was too small over the whole temperature range examined to allow the study of the surface carbon species. Therefore, only the reactivity of the nondissociated, chemisorbed CO could be observed. According to Table 8, the CO pulsed at 300°C produced chemisorbed CO (63% of a monolayer) and C (0.2% of a monolayer). When this sample was cooled to room temperature and subsequently treated with two hydrogen pulses, no hydrocarbons were produced. Subsequent hydrogen pulses at 200°C converted only 5% of this chemisorbed CO to CH_4. Similarly, a chemisorbed CO monolayer adsorbed at room temperature (Table 8) produced no hydrocarbon products upon pulsing with hydrogen at room temperature. Heating this sample to 200°C, followed by a subsequent hydrogen pulse, converted only a 0.5% of the chemisorbed CO to CH_4. In both experiments, substantial hydrogen adsorption was qualitatively observed, which suggests that chemisorption on the metal or complex formation with some of the adsorbed CO is occurring.

2. Study of nickel. Both nickel catalysts, Catalysts B and C, were evaluated for CO disproportionation at temperatures below

TABLE 7

CO and H_2 Pulses over 1.2% Ru/SiO_2 (Catalyst F)[a]

Gas pulsed	Catalyst temperature (°C)	Product (% of monolayer)	Surface layer (% of monolayer)
CO	300	63.0–CO 30.0–CO_2 30.0–C ads. 11.0–CO ads.	41.0
H_2	300	32.0–CH_4	9.0
H_2	300	0.7–CH_4	8.3

[a] Pulse size, 134% of a monolayer.

TABLE 8

CO and H_2 Pulsed over 4.9% Pd/SiO_2 (Catalyst C)[a]

Gas pulsed	Catalyst temperature (°C)	Product (% of monolayer)	Surface layer (% of monolayer)
CO	300	26.0–CO 0.2–CO_2 0.2–C ads. 63.3–CO ads.	63.5
H_2 (two pulses)	23	0	
Heat	200	0.2–C_1	
H_2	200	1.4–CH_4	61.9
H_2 (three pulses)	200	1.8–CH_4	60.1
CO (two pulses)[b]	23	79.6–CO 99.8–CO ads. 0.02–CO_2	100
H_2	23	0	
Heat	200	20.0–CO 0.06–CO_2	80
H_2	200	0.4–CH_4 Trace–C_2	79.6

[a] Pulse size, 89.7% of a monolayer.

[b] The surface was cleaned overnight in flowing hydrogen at 300 to 450°C.

300°C. First, CO was pulsed over Catalyst C at 200°C, which produced 58% of a monolayer consisting of 36% C and 64% CO. A subsequent series of hydrogen pulses at 200°C converted 95% of the surface layer to CH_4 (Table 9).

In a series of experiments with Catalyst B, CO was first adsorbed at room temperature. At this temperature, lack of CO_2 formation showed the absence of CO disproportionation and the absence of surface carbon. When the catalyst covered with a CO monolayer was heated from room temperature to 110°C, a subsequent H_2 pulse produced no hydrocarbon product in the effluent (Table 10). Upon heating to 150°C, the CO monolayer adsorbed at room temperature is reduced to 87% coverage and consists of 98.7% CO and 1.3% C. At this temperature, only 0.3% of the surface layer reacted with a subsequent hydrogen pulse to produce methane. In both of these experiments, unreacted hydrogen was present in the effluent, and the reduced quantity of the hydrogen effluent relative to the size of the hydrogen pulse indicated significant hydrogen adsorption on the sample.

In further work, CO was adsorbed on a Ni/SiO_2 catalyst at 100°C, which resulted in less than monolayer converge and thus allowed free adsorption sites for H_2. The following H_2 pulses at 100°C did not produce any hydrocarbons in the effluent. In a separate experiment, H_2 and CO were introduced together at 100°C over a fresh Ni/SiO_2 sample; however, here again no hydrocarbon product was detected (*24*). Furthermore, when H_2 was introduced at 100°C followed by CO, no products were found in the He stream.

When a fresh CO monolayer adsorbed at room temperature was heated to 200°C, about 23% of the adsorbed CO disproportionated, and 11% desorbed as CO, which resulted in 75% coverage consisting of 15% C and 85% CO, as calculated by CO_2 formation. A subsequent series of hydrogen pulses at 200°C converted over 97% of the surface layer to CH_4 (Table 10).

In contrast to chemisorbed CO, the surface carbon formed at 300°C showed a remarkable reactivity when exposed to H_2 at low temperatures. According to Table 11, at 300°C, a single CO pulse on Catalyst B produced 144% of a surface layer consisting of 22% CO and 78% C. This surface layer was then rapidly cooled to room temperature to prevent aging of the surface carbon. A subsequent H_2 pulse at room temperature converted about 3.5% of the surface layer to hydrocarbons consisting of methane, ethane, propane, and butane, with carbon efficiencies of 42, 46, 11, and 1%, respectively. A second hydrogen pulse at room temperature produced substantially smaller amounts of products. On heating this sample to 80°C, a subsequent hydrogen pulse converted about 9% of the residual surface layer to methane and homologs. Two subsequent hydrogen pulses at 80°C resulted in an additional 10% conversion of the residual surface layer. A further hydrogen pulse at 115°C converted 12.5% of the remaining surface layer to hydrocarbons.

The analysis of the hydrocarbon products obtained at increasing temperatures shows that the hydrocarbons produced contain an increasing fraction of methane, until, finally, at 150 to 200°C, the effluent is 98 to 100% methane. The composition of the hydrocarbons produced is strongly influenced by both the temperature and concentration of the surface layer. The formation of methane homologs increases at the lower temperatures and with higher surface layer concentrations (Table 11).

3. Study of cobalt. The surface layer formed on cobalt showed behavior very similar to that of the nickel surface layer. At ~200°C, the CO pulse produced an 87%

TABLE 9

CO and H_2 Pulsed over 2.7% Ni/SiO_2 (Catalyst C)[a]

Gas pulsed	Catalyst temperature (°C)	Products (% of monolayer)	Surface layer (% of monolayer)
CO	200	285–CO	
		21.0–CO_2	
		21.0–C ads.	58.0
		37.0–CO ads.	
H_2	200	36.0–CH_4	22.0
H_2	200	13.0–CH_4	9.0
H_2 (two pulses)	200	7.2–CH_4	1.8
CO	200	282–CO	
		25.0–CO_2	
		25.0–C ads.	57.0
		32.0–CO ads.	
H_2	200	34.0–CH_4	23.0
H_2	200	13.0–CH_4	10.0
H_2 (two pulses)	200	5.1–CH_4	4.9
CO (two pulses)	200	604–CO	
		42.0–CO_2	
		42.0–C ads.	82.0
		40.0–CO ads.	
H_2	200	49.0–CH_4	33.0
H_2	200	15.0–CH_4	18.0
H_2 (two pulses)	200	7.6–CH_4	10.4

[a] Pulse size, 364% of a monolayer.

TABLE 10

CO and H_2 Pulses over 7% Ni/SiO_2 (Catalyst B)[a]

Gas pulsed	Catalyst temperature (°C)	Product (% of monolayer)	Surface layer (% of monolayer)
CO	23	160–CO	
		102–CO ads	102
H_2	110	0	
CO[b]	23	162–CO	
		100–CO ads.	
Heat	150	12.0–CO	
		1.1–CO_2	
		1.1–C ads. 85.8–CO ads.	86.9
H_2	150	0.3–CH_4	86.6
CO[c]	23	165–CO	
		97.0–CO ads.	97.0
Heat	210	11.0–CO	
		11.0–CO_2	
		11.0–C ads. 64.0–CO ads.	75.0
H_2	200	31.0–CH_4	44.0
H_2	200	23.0–CH_4	21.0
H_2 (four pulses)	200	19.2–CH_4	1.8

[a] Pulse size, 262% of a monolayer.

[b] The catalyst was treated in flowing hydrogen at 480°C for 16 hr.

[c] The catalyst was treated in flowing hydrogen at 480°C for 1.5 hr.

surface layer consisting of 33% C and 67% CO (Table 12). A subsequent series of three hydrogen pulses converted 84% of the surface layer to methane and a small amount of homologs. At room temperature, a CO pulse over Catalyst D produced a monolayer coverage without producing any CO_2, which indicates the absence of CO disporportionation at room temperature. A subsequent hydrogen pulse at room temperature produced no product in the effluent; however, the hydrogen retained on the catalyst indicated substantial hydrogen adsorption, probably via surface complex formation (Table 12). In another experiment (Catalyst E), a fresh CO monolayer adsorbed at room temperature was heated to 110°C. At this temperature, 8% of the surface layer desorbed as CO, and approximately 0.6% disproportionated. A subsequent hydrogen pulse at 110°C produced trace amounts of CH_4, which amounted to only a fraction of the surface C generated through disproportionation (Table 12).

On cobalt, the reactivity of the surface carbon at low temperatures and the product compositions are similar to those observed with nickel (Table 13). The surface carbon formed through CO disproportionation at 300°C was 197% of a monolayer consisting of 94% C and 6% adsorbed CO. Upon cooling to room temperature, about 5% of the surface layer reacted with the first hydrogen pulse, generating methane, ethane, propane, and butane with carbon efficiencies of 49.4, 39.2, 8.4, and 3.0%, respectively. As further hydrogen pulses were introduced and the temperature was raised to 200°C, the activity profile of the surface layer and the composition of the hydrocarbon product were similar to those observed with nickel. Again, the fraction of methane homologs was larger at the lower temperatures and at higher surface coverage.

4. Study of ruthenium. In the case of ruthenium, the surface layer was prepared by pulsing CO over the Ru/SiO_2 sample at 400°C. The obtained surface layer was 57% of a monolayer, and is consisted of 86% C and 14% adsorbed CO. After rapid cooling to room temperature, the initial hydrogen pulse converted about 15% of the surface layer to 81% methane and 19% ethane. Traces of C_3 product were also observed after a subsequent hydrogen pulse. After the room temperature experiments, a H_2 pulse was introduced at 125°C, which

TABLE 11

CO and H_2 Pulses over 7% Ni/SiO_2 (Catalyst B)[a]

Gas pulsed	Catalyst temperature (°C)	Products (% of monolayer)	Percentage carbon distribution in HC products	Surface layer (% of monolayer)
CO	300	4.5–CO		
		113–CO_2		
		113–C ads.		143.5
		30.5–CO ads.		
H_2	23	2.2–CH_4	41.6	141.3
		1.2–C_2H_6	45.5	138.9
		0.2–C_3H_8	11.4	138.3
		0.02–C_4H_{10}	1.5	138.2
H_2	23	0.90–CH_4	68.2	137.3
		0.09–C_2H_6	13.6	137.2
		0.08–C_3H_8	18.2	137.0
Heat	80	0.5–C_1		136.5
H_2	80	8.7–CH_4	72.0	127.8
		1.0–C_2H_6	16.5	125.8
		0.3–C_3H_8	7.5	124.9
		0.24–C_4H_{10}	4.0	124.0
		Trace–C_5H_{12}		124.0
H_2 (two pulses)	80	8.5–CH_4	71.2	115.4
		0.7–C_2H_6	11.7	114.0
		0.4–C_3H_8	10.1	112.8
		0.2–C_4H_{10}	7.0	112.0
		Trace–C_5H_{12}		112.0
H_2	115	10.0–CH_4	69.7	102.0
		1.4–C_2H_0	19.5	99.2
		0.4–C_3H_8	8.6	98.0
		0.08–C_4H_{10}	2.2	97.9
		Trace–C_5H_{12}		97.9
	115	5.3–CH_4	78.9	92.6
		0.4–C_2H_6	12.2	91.8
		0.2–C_3H_8	8.9	91.2
Heat	160	1.0–C_1		90.2
H_2	155	15.0–CH_4	98.2	75.2
		0.1–C_2H_6	1.5	75.0
		0.01–C_3H_8	0.2	74.9
H_2	200	22.0–CH_4	99.7	52.9
		0.02–C_2H_6	0.3	52.9
H_2 (two pulses)	200	9.9–CH_4	100	43.0

[a] Pulse size, 261% of monolayer.

TABLE 12

CO and H_2 Pulses over 7.3% Co/SiO_2 (Catalyst D)

Gas pulsed	Catalyst temperature (°C)	Products (% of monolayer)	Percentage carbon distribution in HC products	Surface layer (% of monolayer)
Pulse size, 312% of a monolayer				
CO (catalyst D)	185	196–CO		
		29.0–CO_2		
		29.0–C ads.		87.0
		58.0–CO ads.		
H_2(3 pulses)	190	70.6–CH_4	97.0	16.4
		0.8–C_2H_6	2.2	14.8
		0.2–C_3H_8	0.8	14.2
Pulse size, 316% of monolayer				
CO (catalyst D)	23	216–CO		100
		100–CO ads.		
H_2	23	0		
Pulse size, 512% of monolayer				
CO (three pulses) (catalyst E)	23	1434–CO		
		0.2–CO_2		
		102–CO ads.		102
Heat	110	7.9–CO		
		0.1–CO_2		94.0
H_2	110	0.05–CH_4		

converted an additional 10% of the residual surface layer to 99% methane and 1% ethane (Table 14).

At room temperature, the CO adsorbed on Ru produced no CO_2 at all, which shows the absence of CO disproportionation and surface carbon formation. Subsequent H_2 pulses at room temperature produced no product in the effluent, although substantial H_2 adsorption was observed.

DISCUSSION

The Reactivity of Chemisorbed CO and Surface Carbon

The absence of CO disproportionation, as demonstrated by the absence of significant amounts of CO_2 in the effluent, shows that the mode of CO sorption on palladium at 300°C is substantially nondissociative. Pulsing hydrogen at 300°C over palladium covered with chemisorbed but nondissociated CO results in instantaneous methane formation. With a single H_2 pulse, one-third of the chemisorbed CO is converted to methane, and subsequent H_2 pulses readily convert over two-thirds of the original adsorbed CO to methane.

In contrast to palladium, on Ni, Co, and Ru, the adsorption of CO at 300°C is substantially dissociative, as indicated by near-complete CO disproportionation. Here, in contrast to palladium, about 70 to 90% of the surface layer consists of surface carbon, and only the remaining 10 to 30% is nondissociated CO. At 300°C, almost the whole surface layer is readily converted to methane by a single hydrogen pulse. When a clean nickel surface is pulsed with CO at 200°C, the surface layer formed consists of about 63% nondissociated CO and 34% surface carbon. A single H_2 pulse at these temperatures converts about 60% of this surface layer to methane. Significantly, the methane formed is substantially more than the amount of surface carbon in the overlayer (Table 9); thus, a significant fraction of the nondissociated CO was also converted to methane.

The pulsing experiment carried out at 200 to 300°C suggested that, in agreement with the conclusion reached by P. R. Wentreek *et al.* (*21*), the surface carbon formed through the dissociation of CO is more reactive to hydrogen than the chemisorbed but nondissociated CO itself. No conclusive proof regarding the relative reactivities of these two species could be

TABLE 13

CO and H_2 Pulses over 7.3% Co/SiO_2 (Catalyst E)[a]

Gas pulsed	Catalyst temperature (°C)	Products (% of monolayer)	Percentage carbon distribution in HC products	Surface layer (% of monolayer)
CO	300	123–CO		
		187–CO_2		
		187–C ads.		197
		10.0–CO ads.		
H_2	23	5.3–CH_4	49.4	191.7
		2.1–C_2H_6	39.2	187.5
		0.3–C_3H_8	8.4	186.6
		0.08–C_4H_{10}	3.0	186.3
H_2	23	2.4–CH_4	66.7	183.9
		0.3–C_2H_6	16.7	183.3
		0.2–C_3H_8	16.7	182.7
H_2	75	11.0–CH_4	71.0	171.7
		1.1–C_2H_6	14.2	169.5
		0.5–C_3H_8	9.7	167.9
		0.2–C_4H_{10}	5.1	167.2
		Trace–C_5H_{12}		
H_2	75	6.6–CH_4	85.7	160.6
		0.4–C_2H_6	10.4	159.8
		0.1–C_3H_8	3.8	159.5
H_2	115°	19.0–CH_4	81.9	140.5
		1.1–C_2H_6	9.4	138.3
		0.4–C_3H_8	5.2	137.1
		0.2–C_4H_{10}	3.5	136.3
		Trace–C_5		
H_2	110	11.0–CH_4	92.8	125.3
		0.2–C_2H_6	5.1	124.7
		0.03–C_3H_8	0.8	124.6
		0.04–C_4H_{10}	1.3	124.5
H_2	160	32.0–CH_4	94.1	92.5
		0.8–C_2H_6	4.7	90.9
		0.1–C_3H_8	0.8	90.6
		0.03–C_4H_{10}	0.4	90.5
H_2	160	12.0–CH_4	96.5	78.5
		0.2–C_2H_6	3.2	78.1
		0.01–C_3H_8	0.2	78.0
H_2	200	14.0–CH_4	99.4	64.1
		0.04–C_2H_6	0.6	64.0

[a] Pulse size, 507% of a monolayer.

TABLE 14

CO and H_2 Pulses over 1.2% Ru/SiO_2 (Catalyst F)[a]

Gas pulsed	Catalyst temperature (°C)	Products (% of monolayer)	Percentage carbon distribution in HC products	Surface layer (% of monolayer)
CO	400	26.0–CO		
		49.0–CO_2		
		49.0–C ads.		57.0
		8.0–CO ads.		
H_2	23	6.9–CH_4	81.2	50.1
		0.8–C_2H_6	18.8	48.5
H_2	23	1.0–CH_4	90.9	47.5
		0.1–C_2H_6	9.1	47.3
		Trace–C_3H_8		
H_2	125	0.5–CH_4	98.9	46.8
		0.03–C_2H_6	1.1	46.7
H_2	400	20.0–CH_4	100	26.7
H_2 (four pulses)	400	5.7–CH_4	100	21.0
CO[b]	23	32.0–CO		
		100.0–CO ads.		100.0
H_2 (two pulses)	23°	0		

[a] Pulse size, 132% of a monolayer.

[b] The surface was cleaned in flowing H_2 at 400°C.

obtained, however, because both of these species are present, and they both react with hydrogen in this temperature range. Therefore, in order to determine unequivocally the relative reactivities of these two species, two different surface layers were prepared for this study. One was obtained by pulsing Ni with CO at room temperature, while the other was prepared by pulsing CO at 300°C. The former consisted of 100% nondissociated CO, while the later contained 80% surface carbon plus 20% nondissociated CO.

When pulsed with H_2 at room temperature, the surface layer consisting of 100% nondissociated CO produced no product in the effluent with any of the metals studied. In addition, with Ni catalyst, even the mixture of CO + H_2 produced no product in the effluent at this temperature. In contrast to chemisorbed but nondissociated CO and the mixture of CO + H_2, the surface layer, consisting mainly of surface carbon, reacted with hydrogen to produce significant amounts of hydrocarbons even at room temperature. These experiments clearly show that the surface carbon formed through disproportionation of CO is much more reactive to hydrogen than the chemisorbed CO itself.

Speculation on the Reaction Mechanism of Hydrocarbon Synthesis

The experimental data presented here describe the mode of CO chemisorption on Co, Ni, Ru, and Pd and show the reactivity of the resulting surface layer to H_2. The mixture CO and H_2 has been used only once to demonstrate that, at room temperature, the CO + H_2 mixture produces no product in the effluent. Consequently, no direct observation was made here on the formation of methane or higher homologs from CO + H_2 gas mixtures.

Even if the data presented here do not deal directly with CO + H_2 synthesis, the relevance of the information to methane synthesis is apparent. It has been shown that, at 300°C, the disproportionation of CO to $CO_2 + C$ over Co, Ni, and Ru is fast and efficient. At this temperature, the freshly formed carbon layer reacts with H_2, forming methane and converting the larger fraction of the whole surface carbon layer to methane in a few seconds. It was also shown that, on Co, Ni, and Ru metals, the surface C species obtained through CO disproportionation is much more reactive to H_2 than the chemisorbed CO itself.

While this information provides no direct proof of the reaction mechanism of methane or, more broadly, of hydrocarbon synthesis over these metals, it inspires the speculation that hydrocarbon synthesis may proceed through a surface carbon reaction intermediate as proposed by Fischer himself (*15*). The principal steps may be envisoned as follows:

$$
\begin{array}{ll}
\text{I} & 2\text{M}(\text{Ni, Co, Ru}) + \text{CO} \rightarrow \text{M–C} + \text{M–O} \\
\text{II-a} & \text{M–O} + H_2 \rightarrow \text{M} + H_2O \\
\text{II-b} & \text{M–O} + \text{CO} \rightarrow \text{M} + CO_2 \\
\text{III} & \text{M–C} + 2H_2 \rightarrow \text{M} + CH_4 \text{ (or homologs)}
\end{array}
$$

The choice between II-a and II-b depends on the reactivities of the M–O species toward H_2 and CO, respectively. Since in most cases the M–O is more reactive to H_2, the production of H_2O dominates.

The results of the pulsing experiments also indicate that the envisioned surface carbon route is probably not the only reaction path to hydrocarbon synthesis. The efficient conversion of mixed overlayers consisting of both surface carbon and nondissociated CO to hydrocarbons (Tables 9 and 12) suggests that the chemisorbed but nondissociated CO is also converted to hydrocarbons. The efficiency of this later route however, appears to be substantially lower than the one observed in the hydrogenation of surface carbon.

The best example of methane synthesis through nondissociated CO may be the palladium. Here, in spite of 99% nondissociated CO in the surface layer, one-third of the surface layer is converted to methane in the first H_2 pulse. It maybe that the conversion of nondissociated CO to hydrocarbons over Ni, Co, Ru, and Pd follows a similar reaction path. The existence of two competing reaction paths to hydrocarbon synthesis over Ni, Co, and Ru no doubt increases the complexity of kinetic behavior and renders kinetic analysis difficult.

The speculation about the reaction mechanism of hydrocarbon synthesis based upon the concentration and reactivity of the potential reaction intermediates has its limitations. For example, the observed large concentration of nondissociated CO on Pd does not rule out the surface carbon reaction path. Namely, if the reactivity of the surface carbon is much higher than that of the nondissociated CO and if the equilibration between surface carbon and chemisorbed CO is fast, then the surface carbon path could apply to Pd as well.

The principal limitation of this speculation on the reaction mechanism is that the catalytic interaction of the actual reaction mixture ($CO + H_2$) has not been studied except at room temperature where no product formation was observed. Furthermore, it is unfortunate that because of experimental difficulties, no data are available which would prove unequivocally the superior reactivity of surface carbon over chemisorbed CO at the higher temperatures which are more relevant to hydrocarbon synthesis. Nevertheless, we feel that this hypothesis is reasonable and useful to the extent that it points to questions in need of further clarification.

A Pattern of Catalytic Properties of Group VIII Metals in $CO + H_2$ Synthesis

The speculation advanced above on the mechanism of hydrocarbon synthesis may help to explain some of the differences in the catalytic behavior of Group VIII metals. For example, the high activity of Co, Ni, and Ru for hydrocarbon synthesis may be explained on the basis of high reactivity to dissociate CO. In contrast to these metals, Pd has very low activity for hydrocarbon synthesis. In this case, low catalytic activity corresponds to only marginal activity to dissociate CO. The data presented in the previous section show that nondissociated CO chemisorbed on Pd is also converted by hydrogen to methane, but at a lower rate relative to surface carbon. This observation may explain the low catalytic activity of Pd as a result of the low chemical efficiency of the reaction path leading through the direct hydrogenation of nondissociated CO.

Poutsma *et al.* (*25*) have recently shown that, under pressure, Pd and Pt, as well as Ir, have excellent catalytic activity for methanol synthesis. At 12 atm and 290°C, with a $CO:H_2$ feed ratio of 30:70, the supported palladium produced methanol of high purity with only very small amounts of hydrocarbon byproduct. Under pressure, the selectivity of Pt and Ir is similar to that of Pd, but their methanol productivity is about an order of magnitude less than that of palladium. In contrast to Pd, Pt, and Ir, a supported-Ni catalyst, similar to the ones used in this study, when tested at 12 atm and 290°C, produced only hydrocarbons (mainly methane) without even a trace of methanol present.

These studies reveal an interesting aspect of the catalytic chemistry of Group VIII metals in syn–gas catalysis. It appears that metals which readily dissociate CO produce mainly hydrocarbons, while those which do not dissociate CO produce methanol. This fundamental, but simplistic, description of catalytic behavior, however, is complicated by several factors reflecting differences in the chemistry of the individual members of Group VIII elements. The well-known differences among Ni, Co, Fe, and Ru in product formation (methane, higher hydrocarbon homologs, and terminal alcohols) and especially the extent of hydrocarbon chain growth may reflect differences in ability to insert CO, CH_x groups, or even product molecules (olefins, alcohols), into the growing hydrocarbon chain efficiently. For example, insertion of CO onto the growing $M–C_xH_y$ chain without subsequent dissociation of the C–O bond may become a chain-terminating step leading to terminal alcohols and aldehydes.

With Pd, Pt, and Ir, the excellent catalytic activity for methanol synthesis may be explained on the basis that these metals provide no efficient path to hydrocarbon synthesis. They do not dissociate CO at moderate temperatures (*18*), and the synthesis of hydrocarbons via direct hydrogenation of nondissociated CO appears inefficient. Thus, in contrast to Co, Ni, and Ru, the excellent hydrogenation activity of Pd, Pt, and Ir dominates catalytic behavior, and the chemisorbed CO is "simply" hydrogenated to CH_3OH. At this point, it is of interest to compare the latter group of metals with oxide-type methanol catalysts such as ZnO and $CuO–ZnO–Cr_2O_3$. One may sepeculate that these transition metal oxides, having their affinity to oxygen already satisfied, probably do not dissociate CO. Since these oxides have good hydrogenation activity, they probably meet the two important criteria demonstrated for Pd: hydrogenation activity coupled with nondissociative CO chemisorption.

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