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Low-Temperature Methanation and Fischer–Tropsch Activity over Supported Ruthenium, Nickel, and Cobalt Catalysts

It has been shown previously that surface carbon derived from the dissociation of CO on supported ruthenium, nickel, and cobalt catalysts at temperatures in excess of 423 K can be hydrogenated to methane at room temperature (*1–3*). However, methanation activity for CO adsorbed at ambient temperatures on these catalysts has not been observed (*1, 2, 4–7*). Here we report methane formation from CO adsorbed under H_2 and hydrogenated at ambient temperature (298–307 K) on supported ruthenium, nickel, and cobalt catalysts. Hydrocarbon chain growth on ruthenium at a slightly higher temperature (324 K) is also reported. A sensitive stopped-flow gas chromatographic reactor technique (*8, 9*) was employed to measure the small rates of reaction at these temperatures.

The flow system for our investigations featured a short catalyst bed (0.4 to 0.8 g catalyst) connected directly in series with an analytical chromatographic column (Chromosorb 102) across an eight-port chromatographic valve (Valco Instr.). A hot-wire thermal conductivity detector and a flame ionization detector were employed in series at the outlet of this system. Rotation of the eight-port valve allowed the hydrogen carrier gas flow to be stopped over the catalyst bed by sealing both ends of the reactor/analytical column loop, while hydrogen flow continued through a balancing bypass restrictor and through the detectors. Stopped-flow experiments were initiated by introduction of one or more 1.1-ml pulses of CO via a six-port valve, with the catalyst bed maintained isothermally between 298 and 498 K. Carbon monoxide was irreversibly adsorbed on the catalyst surface and reacted slowly at room temperature. Following initiation, the flow of hydrogen was stopped over the catalyst bed for 1 min every 5 min, generating sharp, stopped-flow product peaks (Fig. 1). These peaks were swept into the analytical column upon resumption of flow, for resolution into C_1 through C_4 hydrocarbon products. Rates of methanation and higher hydrocarbon synthesis were determined from stopped-flow peak areas (flame ionization detector response) as the layer of adsorbed CO was depleted via reaction.

The 5% Ru/Al_2O_3, 8.6% Ni/Al_2O_3, and 25% Co/kieselguhr catalysts used here were obtained from Strem Chemicals. Catalyst charges were reduced for 4 h under H_2 at 673 K before use. Metal dispersions were determined by pulse injections of CO under helium at 373 K (dynamic pulse method (*10*)) with an assumption of one CO molecule per exposed metal surface atom.

Rates of methane formation measured by the stopped-flow technique are plotted

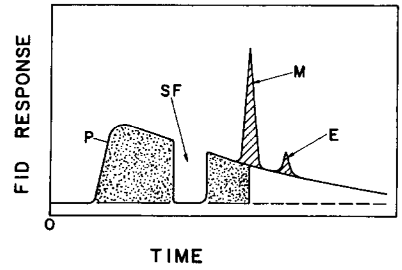

FIG. 1. Stopped-flow reaction chromatogram. Injection of CO pulse under hydrogen-generated reaction profile (P). Stopped-flow produced FID baseline disruption (SF), followed by superimposed stopped-flow product peaks for methane (M) and ethane (E). Areas under the sharp stopped-flow peaks represent product formation during 1-min stopped-flow interval, SF.

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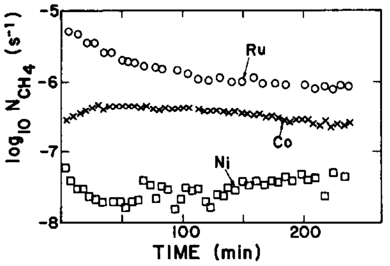

FIG. 2. Methanation rates measured by stopped-flow. Rates were measured via 1-min stopped-flow intervals following injection of CO at time = 0. Catalyst dispersions reported in Table 1. Ru—298 K, Co—307 K, Ni—305 K, N_{CH_4}—turnover frequency for methane formation.

against time in Fig. 2. These experiments were initiated by injection of a single 1.1-ml pulse of CO under hydrogen between 298 and 307 K. The amount of CO initially adsorbed ranged from 1.0 to 1.2 monolayers, with a monolayer defined as the amount of CO irreversibly adsorbed under helium in dynamic pulse experiments. The total amount of methane formed during a 4-h stopped-flow experiment over ruthenium corresponded to conversion of 0.03 monolayers of initially adsorbed CO. Four-hour experiments over cobalt and nickel catalysts gave total conversions of approximately 0.01 monolayers. These values are two orders of magnitude greater than that which could have resulted from trace hydrocarbon impurities in the injected pulse. Stopped-flow blanks were effected immediately before the injection of CO to insure that observed activities were not confounded by hydrocarbon impurities accumulated on the surface during pretreatment and stabilization under H_2. These tests established that the methane formation reported in Fig. 2 did indeed result from carbon monoxide conversion.

The low-temperature experiments of Fig. 2 indicate a relative ordering of methanation activity Ru > Cu > Ni somewhat different from the trend in "intrinsic" activities for these metals under steady-state reaction conditions at 548 K reported by Vannice (*11*), who found nickel more active than cobalt. The enhanced activity of our cobalt catalyst may have resulted from use of the kieselguhr support containing traces of iron, and the very low dispersion (1%) of this catalyst. For direct comparison with the relative activities of our catalysts at higher temperatures, supplemental pulse microreactor experiments were conducted. A series of pulse microreactor experiments at 494 K involving measurement of the fractional conversion of 1.1-cm^3 CO pulses over the ruthenium, nickel, and cobalt catalysts indicated the same order of activity as that observed for stopped-flow experiments at 298–307 K (Table 1).

Higher hydrocarbon formation was also observed at low temperatures using the stopped-flow technique. C_2 formation was evident at 298 K for experiments over the Ru/Al_2O_3 catalyst. At 324 K, C_1 through C_4 hydrocarbons were formed in measurable quantities over this catalyst. As the number of CO pulses injected to initiate a stopped-flow experiment was increased from 1 to 10 and then 30, the selectivity to higher hydrocarbon formation increased with a chain-growth probability shown in Table 2. Rates of formation of hydrocarbons for a stopped flow experiment initiated with 30 pulses of CO at 324 K are shown in Fig. 3. The CO adsorbed following injection of the first pulse exceeded one monolayer; evolution of hydrocarbon products was negligible during the CO pulsing. This reflects suppression of hydrogenation reactions by the high coverage of adsorbed CO and related species in the presence of excess gaseous

TABLE 1

Pulse Microreactor Experiments at 494 K

Catalyst	Dispersion	$N_{CH_4}{}^a$ (sec^{-1})
5% Ru/Al_2O_3	0.20	1.27
25% Co/kieselguhr	0.01	0.78
8.6% Ni/Al_2O_3	0.04	0.14

[a] Turnover frequency estimated from conversion of single CO pulse in a hydrogen carrier gas.

TABLE 2

Probability of Chain Growth for Stopped-Flow Experiments over Ru/Al_2O_3 at 324 K

Number of CO pulses injected for initiation	Chain-growth probability[a]	Products observed
1	0.04	C_1–C_3
10	0.09	C_1–C_3
30	0.24	C_1–C_4

[a] Chain-growth probability here is the slope of a plot of $\ln(N_{C_n})$ versus carbon number (n) extrapolated to beginning of stopped-flow experiment, where N_{C_n} is the turnover frequency for formation of products containing n carbons.

CO. Thus, chain growth continued during repeated pulsing of CO at low temperatures, during which time the total moles of adsorbed carbon (including CO and species derived from CO) exceeded one monolayer.

The significance of the low-temperature activities reported here lies in possible implications concerning adsorption and surface reaction phenomena. Recent correlations between dissociative adsorption of CO and methanation/Fischer–Tropsch activity have supported arguments for the participation of carbidic or CH_x intermediates in these reactions (*1–7*). However, surface spectroscopy has indicated that CO is molecularly (nondissociatively) adsorbed on Ru, Ni, and Co at room temperature in some instances up to or above 376 K (*12–16*). In temperature-programmed desorption and pulse microreactor experiments, CO disproportionation (for which CO dissociation may be a rate-limiting step) has not been observed over these catalysts below approximately 423 K (*1, 2, 4, 7, 17*). Thus, the present observation of methanation and chain-growth activity at temperatures below those for which CO dissociation has been previously established suggests the possibility of the direct participation of molecularly adsorbed CO in these reactions (*18–21*).

However, our results also are consistent with the premise that a single reaction path is operative at both high and low temperatures (298–494 K) and that CO dissociation does occur over these catalysts at low temperatures, albeit at levels difficult to detect. Group VIII metal surfaces with a high concentration of coordinately unsaturated kink or step atoms have demonstrated unusual activity for the dissociation of CO (*22, 23*). These sites (representing a fraction of the total surface of our supported metal catalysts) could produce carbidic or CH_x intermediates from adsorbed CO to account for the observed levels of methanation and chain-growth activity at room temperature via reaction pathways currently favored for higher-temperature operating conditions (*24–26*). The following observations support the hypothesis that similar mechanisms are responsible for the room-temperature activities reported here:

(1) The relative ordering of methanation activities for our nickel, ruthenium, and cobalt catalysts at room temperature is in agreement with that at higher temperature (494 K).

(2) The methanation activation energies estimated from our stopped-flow and pulse microreactor experiments are in the range 20 to 26 kcal/g mole (over about 195 K) in broad agreement with other values of apparent activation energies determined by using power-law models for higher-temper-

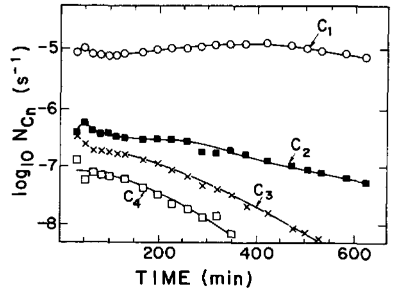

FIG. 3. Hydrocarbon formation in stopped-flow Fischer–Tropsch experiment over Ru/Al_2O_3 catalyst (0.4 g) at 324 K. Experiment intitated at 324 K with thirty 1.1-ml pulse CO injections in 25 ml/min carrier gas. Rates were measured using 1-min stopped-flow intervals.

ature steady-state experimental data (*11, 27, 28*).

The low-temperature methanation activity reported here illustrates additional catalytic applications of the sensitive stopped-flow chromatographic reactor (*9*). Reaction products are concentrated during stopped-flow intervals before being swept directly to on-line detectors for analysis. Thus, sampling for analysis in a separate system is not necessary, and very low rates of reaction can be measured.

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