Heterogeneous Methanation: Initial Rate of CO Hydrogenation on Supported Ruthenium and Nickel

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The initial rate of reaction of hydrogen and carbon monoxide was measured on supported Ru and Ni catalysts in a differential batch reactor. Using hydrogen adsorption to determine Ru and Ni surface areas, initial rates for methane and total hydrocarbon formation were expressed as turnover numbers.

The initial rate of supported ruthenium was found to be independent of ruthenium particle size from <10 to 90 Å. Nickel exhibited turnover numbers twice as high as Ru at 280°C and activation energies of 20 and 28 kcal mole^{-1} for total hydrocarbon and methane formation compared to 17 and 24 kcal mole^{-1} for Ru.

INTRODUCTION

The scarcity of fluid forms of fossil fuel and the relative abundance of coal has recently refocused attention on the conversion of the latter to oil and gas. One of the major steps in the conversion of coal into pipeline quality gas is the production of methane from hydrogen and carbon monoxide (synthesis gas) produced in the gasification of coal.

The highly exothermic nature of the hydrogenation reaction, the high percentage of synthesis gas in the gasified effluent and the high space velocities in proposed coal gasification plants place stringent demands on the methanation catalyst. No commercial size methanation reactor is fully operational at present. Proposed systems include supported iron and nickel catalysts, and high-surface-area Raney nickel plated onto heat exchange tubes (*1*). Sulfur is present in significant quantities in coal (1–4%) and is carried into the gasified effluent. The need to remove most of the sulfur to achieve the low levels required for the survival of the methanation catalyst represents a significant cost in the production of pipeline quality gas (*2*). These factors make the hydrogenation of CO an area where there is considerable practical importance in further efforts to develop new catalysts with better resistance to high temperature, better selectivity for methane production and greater resistance to sulfur poisoning.

There have been a number of studies of catalytic hydrogenation on iron and nickel and, to a lesser extent, on cobalt and ruthenium. An extensive review by Mills and Steffgen (*3*) has been published recently. Early work with Ru included the synthesis of high molecular weight paraffins at high pressure and of methane at low pressure (*4–6*). Guyer *et al.* (*7, 8*) studied the hydrogenation of CO at high pressures on MgO-promoted Ru catalysts. The observed variation in product distribution was ascribed to a variation in the catalyst pore distribution. Karn, Schultz and Anderson (*9*) examined this reaction on supported Ru at moderate pressures and observed quite high methane yields. The removal of small quantities of CO and CO$_2$ from hydrogen has been widely studied as a means to purify hydrogen for use in ammonia synthesis. In this process CO is found to react selectively in the presence of CO$_2$ (*10, 11*). More recently McKee (*12*) reported work on adsorption and ini-

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tial reaction rates for CO and H_2 on unsupported Ru.

However, there are no published data on Ni and Ru activity under the same experimental conditions obtained in a differential reactor. This paper presents results obtained for the initial rate of CO hydrogenation on a series of supported ruthenium catalysts of varying particle size. The initial rate on a supported nickel catalyst was also measured. The initial rate is most representative of the activity of a clean surface and differs considerably from the activity under steady state conditions. Previous comparisons relate primarily to the latter.

EXPERIMENTAL METHODS

Apparatus

Adsorption measurements were performed with a conventional Pyrex glass constant-volume adsorption system equipped with greased high-vacuum stopcocks. The pumping system consisted of an oil diffusion pump and a rotary mechanical pump isolated from the adsorption system by liquid-nitrogen cooled traps. Adsorbate gases were purified and placed in 5 and 12 liter glass bulbs for future use. Pressure was measured with a Texas Instruments quartz spiral Bourdon gage. The catalyst sample was placed in a flow-through cell to permit reduction in a flowing hydrogen stream prior to the adsorption measurements.

Reaction rates were measured in a Pyrex batch recycle reactor using a reciprocating glass pump similar to that described previously (13). The circulation rate was approximately 400 cc min^{-1} in a system volume of 530 cc. Pressures were measured with a Dynasciences pressure transducer. The reacting gases passed through a gastight small-volume injection valve connected to a gas chromatograph equipped with a flame ionization detector. The injected gas sample, approximately 0.4 cc, was split into two streams; one half was analyzed for methane by separation over a 3 m column of 5A molecular sieve, and the other half passed directly to the detector.

Known pressures of pure methane were used to calibrate the system.

Materials

The five supported Ru and Ni catalysts were prepared as follows. The 1.5% Ru/Al_2O_3 and the 5% Ru/Al_2O_3 catalysts were prepared by impregnation of Dispal M alumina (Continental Oil Co.) with sufficient ruthenium trichloride solution to fill the support pore system without causing the catalyst to appear wet. A small amount of nitric acid had been added to the ruthenium solution to prevent hydrolysis and precipitation of the ruthenium. After impregnation, the sample was dried in air at 80°C. In the case of the 0.1% Ru–3% La/Al_2O_3 catalyst, 3 mm low density alumina beads from Universal Oil Products were impregnated first with a La$(NO_3)_3$ solution to saturate the beads. The alumina was then dried at 100°C and calcined in air at 600°C for 2 hr. The ruthenium was then added in a similar manner and the sample dried at 100°C. A commercial catalyst obtained from Engelhard Industries, 0.5% Ru on 3 mm alumina pellets, was also used. This catalyst was ground in a mortar to a fine powder. Small portions were pressed at 1.4×10^8 N m^{-2} and sieved. The fraction from 0.5 to 2 mm particle size was used for adsorption measurements. The powdered Dispal-supported catalysts were pressed and sieved in a similar manner. In preparing the Ni/ZrO_2 catalyst, colloidal zirconia from the TAM Division of N. L. Industries was dried in air at 70°C and the resulting solid was lightly ground in a mortar. The powdered zirconia was then calcined at 500°C in air for 12 hr. Nickel was introduced by impregnation with nickel nitrate as described for the Ru/alumina catalysts.

Matheson research grade CO, 99.99% pure, was used without further purification. Commercial hydrogen of 99.95% purity was passed through an Engelhard palladium Deoxo catalytic purifier and dehydrated over 5A molecular sieve at −196°C before use. Ultrahigh purity (99.97%) methane from Matheson Co. was used as

received for calibrating the gas chromatograph.

Adsorption Measurements

Prior to adsorption measurements the samples were first reduced in hydrogen, flowing at 100 cc min⁻¹, at 450°C for 2 hr and then evacuated at 450°C for another 2 hr. Hydrogen adsorption isotherms were measured over a pressure range of 6.7×10^3 to 4.4×10^4 N m⁻² (1 Torr = 133.3 N m⁻²) and the linear portion above 2.0×10^4 N m⁻² extrapolated to zero pressure to obtain the hydrogen adsorption on ruthenium (14). These data are presented in Table 1. As discussed in a previous publication (14) a 1:1 correspondence between H adsorbed and surface ruthenium atoms is assumed. The particle size is calculated assuming an area per surface ruthenium of 8.17 Å² and the particle to be cubic, with five sides exposed to the gas phase. A hydrogen adsorption isotherm was measured on the Ni/ZrO$_2$ catalyst in a manner similar to that described for Ru (15, 16). The particle size was calculated taking an area of 6.76 Å²/surface nickel atom.

Kinetic Measurements

The catalyst samples used in the hydrogen adsorption experiment, generally 1 g, were ground and sieved. Samples of 10 to 100 mg of the 100–150 mesh fraction were used for the rate measurements. The

catalysts were reduced in flowing H$_2$ at 100 cc min⁻¹ for at least 2 hr at 450°C before the temperature was lowered to the reaction temperature. Before the catalysts were exposed to the reaction mixture, the reactor was evacuated for 1 min, to a residual pressure of approximately 7 N m⁻². After a rate measurement, the reactor was purged with H$_2$ and heated to 450°C for at least 2 hr before subsequent kinetic runs. The initial activity was very reproducible after such a treatment.

Typical conversion versus time curves for total HC and CH$_4$ formation, and the initial rate calculated for the purposes of this study (solid lines) are shown in Fig. 1. As seen from the data points, the rate of hydrogenation of CO on ruthenium deteriorated rapidly on all catalysts. Since initial rates would be most representative of the metal surface and particle size defined by the adsorption measurements, the rate was taken from conversion versus time data for times less than 1000 s. The specific rates are expressed as turnover numbers, N, in units of reciprocal seconds (s⁻¹), i.e., molecules of product formed per 1 surface Ru atom/s.

Initial rates determined in this manner

TABLE 1
HYDROGEN ADSORPTION DATA

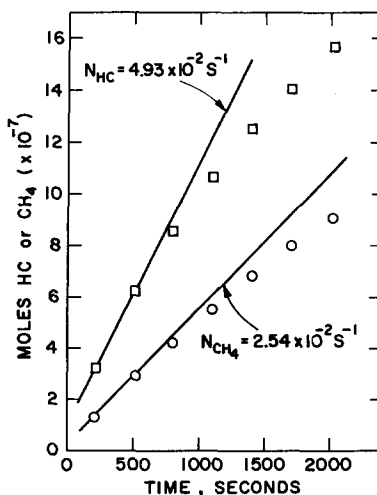| Sample	H$_2$ adsorption (μmoles g⁻¹)	Dispersion (H$_{ads}$/M$_{total}$)	d (Å)
0.1% Ru–3% La/Al$_2$O$_3$	5.1	1.03	<10
0.5% Ru/Al$_2$O$_3$ (Engelhard)	16.0	0.65	16
1.5% Ru/Al$_2$O$_3$	25.6	0.35	24
5% Ru/Al$_2$O$_3$ (heat treated)	22.8	0.092	91
5% Ni/ZrO$_2$	33.7	0.079	102

FIG. 1. CO hydrogenation at standard conditions on 0.0455 g of 5% Ru/Al$_2$O$_3$ (heat treated) at 280°C. (□) Total HC formation; (○) CH$_4$ formation.

were measured for three Ru/Al$_2$O$_3$ catalysts of widely different metal particle size over the temperature range of 190–330°C (Fig. 2). Standard reaction conditions were chosen to approach actual use conditions and to be compatible with our recirculating glass batch reactor. A synthesis gas pressure of 0.75 atm, with a H$_2$:CO ratio of 3 was chosen. The H$_2$ and CO pressures were 5.70 × 10^4 N m^{-2} (0.5625 atm) and 1.90 × 10^4 N m^{-2} (0.1875 atm), respectively. The solid lines in Fig. 2 were obtained by least squares fit of the data on the 1.5% Ru/Al$_2$O$_3$ catalyst and gave apparent activation energies of 17 kcal mole^{-1} for total hydrocarbon production and 24 kcal mole^{-1} for methane formation. The points for the other catalysts of larger and smaller Ru metal particle size fall close to these straight lines. The broken lines for data obtained above 280°C on the 0.5% Ru/Al$_2$O$_3$ (Engelhard) catalyst are discussed below.

The rate of hydrogenation of CO was also measured using an entirely different catalyst of low ruthenium concentration, 0.1% Ru–3% La/Al$_2$O$_3$. This catalyst had a very high dispersion, near unity, but gave measured initial reaction rates identical to those found on the other catalysts over the entire temperature range studied, 220–320°C.

To help establish the effect of higher hydrocarbons on the rate of methane formation several experiments were run with a liquid-nitrogen cooled trap in the recirculation system downstream of the reactor. This trap removed 92% of the hydrocarbons, other than methane, formed during the reaction. On the 1.5% Ru/Al$_2$O$_3$ catalyst, at 260°C and standard CO and H$_2$ pressures, the change in methane concentration with time and the calculated initial rate of methane formation were identical to those determined in a run without the liquid-nitrogen trap in place.

The dependence of the reaction rate on reactant pressure was measured at 240 and 300°C on the 1.5% Ru/Al$_2$O$_3$ catalyst over a CO pressure range of 2 × 10^3 to 5 × 10^4 N m^{-2} and a H$_2$ pressure range of 1 × 10^4 to 1 × 10^5 N m^{-2}. The data for 300°C are shown in Fig. 3.
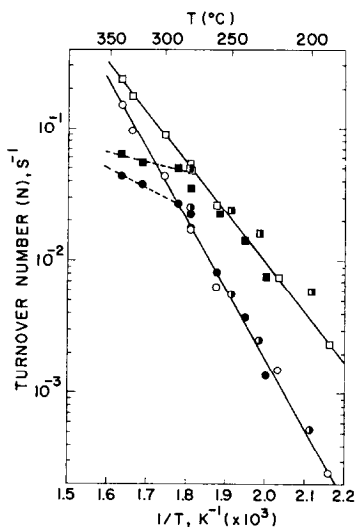
A power rate law of the form,

FIG. 2. Arrhenius plot of CO hydrogenation rate at standard conditions for (□) total HC formation and (○) CH$_4$ formation: (□, ○) 1.5% Ru/Al$_2$O$_3$; (■, ●) 0.5% Ru/Al$_2$O$_3$, Engelhard; (◪, ◑) 5% Ru/Al$_2$O$_3$ (heat treated).
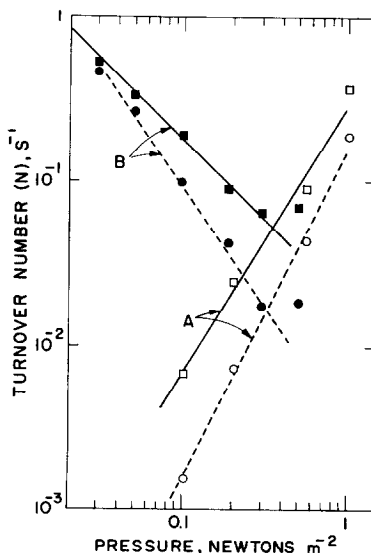
FIG. 3. Dependence of the reaction rate at 300°C: (A) on hydrogen pressure at P_{CO} = 1.90 × 10^4 N m^{-2} and (B) on CO pressure at P_{H_2} = 5.70 × 10^4 N m^{-2}. (□, ■) Total HC formation; (○, ●) CH$_4$ formation.

$$r = r_0 \left[\frac{P}{P_0}\right]_{H_2}^n \left[\frac{P}{P_0}\right]_{CO}^m,$$

is assumed, where P_0 and r_0 are the pressure and reaction rate at standard conditions. The values of n and m given in Table 2 where obtained by least squares fitting of the data. The reaction rate is constant with respect to CO pressure above $P_{CO} = 2.0 \times 10^4$ N m^{-2} at 240°C and above $P_{CO} = 3.0 \times 10^4$ N m^{-2} at 300°C.

In several cases, during the course of several experiments on a given catalyst, the initial reaction rate was observed to increase 2- to 4-fold over the rate on the fresh sample. These higher rates were not affected by reduction of the catalyst in H$_2$ at 450°C for prolonged periods or by further reaction of H$_2$ and CO. Most such occurrences were preceded by exposure or possible exposure of the hot catalyst to air or oxygen. Such treatment could lead to surface roughening or redispersion of the ruthenium, a possibility supported by recent observations of Taylor, Sinkevitch and Klimisch (17) where several reactions including the hydrogenation of CO were found to increase in rate after treatment in oxygen. Similar behavior for supported platinum was shown to be due to an increase in surface area after high temperature oxygen treatment (18).

The initial rate of CO hydrogenation at the standard conditions was studied over the temperature range 200–280°C on the 5% Ni/ZrO$_2$ catalyst listed in Table 1. The reaction rate on this nickel catalyst also decreased with time as was observed for Ru. The initial reaction rates as a function
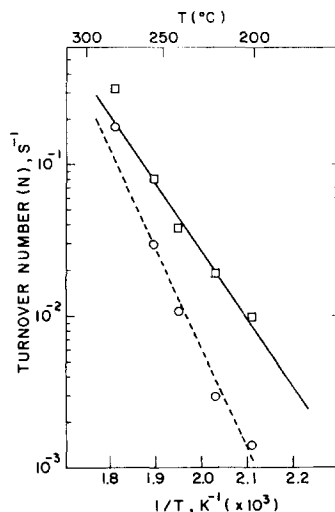

FIG. 4. CO hydrogenation rate at standard conditions for (□) total HC formation and (○) CH$_4$ formation on 5% Ni/ZrO$_2$.

of $1/T$ are presented in Fig. 4. Above 280°C the high reaction rate could lead to heat transfer effects causing the high points. The calculated apparent activation energies are 20 and 28 kcal mole^{-1} for total HC and CH$_4$ production, respectively.

DISCUSSION

The rate of reaction of hydrogen and carbon monoxide decreases rapidly with time on a clean ruthenium surface. Nevertheless, an initial rate can be obtained from the conversion versus time curve by determining the slope in a consistent manner at short times. This initial rate gave a linear Arrhenius plot from 190–340°C for the 1.5% Ru/Al$_2$O$_3$ catalyst (Fig. 2). Apparent activation energies of 17 kcal mole^{-1} for total hydrocarbon formation and 24 kcal mole^{-1} for methane formation can be compared with the value of 9 kcal mole^{-1} obtained by McKee (12) for the initial rate of methane formation on unsupported ruthenium. No comparison of the absolute initial rates could be made with the work of McKee as the units of the rate were not defined by the author in an unambiguous fashion.

The specific reaction rate, expressed as a turnover number, correcting for Ru sur-

TABLE 2

REACTION ORDERS FOR INITIAL RATES
ON 1.5% Ru/Al$_2$O$_3$

Temp (°C)	Exponent	Product	
		Total HC	CH$_4$
240	n	1.28	1.79
	m	−0.47	−1.14
300	n	1.70	2.04
	m	−0.93	−1.43

face area determined by hydrogen adsorption, was found to be constant on all ruthenium catalysts listed in Table 1. Within this group of catalysts, the metal particle size varies from <10 to 90 Å in diameter. In this particle size range, the metal crystallite would exhibit large variations in coordination number of its surface atoms (19). Thus this reaction would be considered a facile or structure insensitive reaction according to Boudart (20).

One sample, the 0.5% Ru/Al_2O_3 Engelhard catalyst, exhibited a break in the Arrhenius curve at 280°C. The low rates above 280°C are probably due to mass transfer limitations caused by two factors. The Al_2O_3 used in the Engelhard catalyst had smaller pores than the Dispal Al_2O_3 used in the other samples, and the Ru in this pelleted commercial catalyst was concentrated near the external surface. Thus this catalyst possessed a high metal concentration in a support pore system of smaller pore diameter compared to the other catalysts tested.

The pressure dependence of the reaction rate found here, negative for CO and positive for hydrogen, has been obtained for Ru catalysts under various conditions by other authors. Karn, Shultz and Anderson (9) at pressures up to 21 atm found a rate law of the form,

$$r = kP_{H_2}^{1.33}P_{CO}^{-0.13},$$

to fit steady state data obtained on a 0.5% Ru/Al_2O_3 catalyst. McKee (12) found $n = 1.94$ and $m = 0$ at 150°C for the initial rate on unsupported ruthenium. Similar orders are also found for CO hydrogenation on nickel where $n = 1.4$ and $m = -0.9$ (21). Such a pressure dependence of the reaction rate, negative for CO and positive for hydrogen, is indicative of a surface with a high CO coverage. Saturation of the surface with CO appears to occur above a partial pressure of 0.2 atm at 240°C and above 0.3 atm at 300°C, resulting in the leveling of the reaction rate observed in Fig. 3.

The high surface coverage by CO during the reaction explains the lack of a significant contribution to the rate of methane formation by hydrogenolysis of higher hydrocarbons. The removal of 92% of the higher hydrocarbons caused no change in the rate of methane formation. The data of Sinfelt (22) can be used to calculate the expected hydrogenolysis rate in the absence of CO. Under the conditions used here, $P_{H_2} = 5.70 \times 10^4$ N m^{-2}, a partial pressure of all hydrocarbons, excluding methane, of 2×10^2 N m^{-2} and a temperature of 260°C, the calculated hydrogenolysis rate on Ru is 3 s^{-1}. This rate is several orders of magnitude larger than the observed rate of CO hydrogenation, implying a complete inhibition of the hydrogenolysis reaction by the presence of CO.

When evaluating the lack of an effect of Ru metal particle size on the reaction rate, recent data from this laboratory (23) on CO adsorption on supported Ru catalysts should be mentioned. These results show that CO adsorption on low-coordination edge and corner sites is weaker than that on a plane face and that multiple CO adsorption occurs, producing species such as $Ru(CO)_2$ at the surface. The presence of a large proportion of such surface sites in the smallest particle size catalyst examined in this work, together with the absence of a particle-size effect in the hydrogenation implies that CO adsorption is not a rate-determining step. The large hydrogen isotope effect obtained by McKee (12) for this reaction and the positive rate dependence on the H_2 pressure indicate H_2 adsorption or its subsequent surface reaction may be rate controlling.

The results on the supported Ni catalyst show that the initial specific rate of CO hydrogenation on Ni is twice as high as Ru at 280°C. Furthermore, as a result of the higher activation energy of 20 kcal mole^{-1} for HC production, Ni should have a higher initial specific rate than Ru at temperatures above 280°C. Catalyst deactivation by coking or other processes may alter this trend. Bousquet and Teichner (21, 24) reported the initial rate of CO hydrogenation on Ni with which the present data can be compared. Assuming a surface nickel atom area of 6.76 Å^2, a turnover number at 300°C can be estimated

making appropriate correction for the reported dependence on CO and H_2 pressure. At the standard conditions used here, the rate calculated from the data of Bousquet and Teichner is 0.16 s^{-1} while the rate determined in this work is 0.21 s^{-1}, which is good agreement.

A comparison of the turnover numbers in the heterogeneous hydrogenation of CO by Ni and Ru has been completed. Since these represent initial rates and not steady state conditions prevailing in industrial installations, it is important to carry this comparison further. Such work is being pursued in our laboratory, first to determine steady state rates for both Ru and Ni catalysts and secondly to establish the rates under conditions where sulfur compounds are present in the reaction mixtures.

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