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SHIFT CONVERSION AND METHANATION IN COAL GASIFICATION:
BENCH-SCALE EVALUATION OF A SULFUR-RESISTANT CATALYST

Final Report

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October 24, 1980

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SRI International
Menlo Park, California

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DOE Contract DE-AC21-78ET11030
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SUMMARY

Reduction of the sulfur level in catalytic methanator feedstocks to the sub-ppm level, required for long-term performance of conventional nickel catalysts, represents an expensive process step. The availability of a catalyst that can operate effectively at higher sulfur levels would substantially reduce purification requirements, and thus reduce the complexity and cost of substitute natural gas (SNG) plant.

Prior laboratory-scale studies have established that the addition of small amounts (< 1 wt%) of iridium to an alumina supported nickel catalyst, enhances its activity for methanation and renders it less susceptible to deactivation by sulfur-bearing compounds. To assess further the suitability of this catalyst for use in SNG manufacture, additional quantitative data on reaction kinetics and deactivation rate were required. Consequently, the study described in this report was undertaken. The objective of the work was to test the catalyst in bench-scale reactors under plant conditions and to provide basic data for scale-up and process design.

Methanation kinetics were measured in a gradientless (internal recycle) reactor for fresh catalyst and for catalyst samples partially deactivated by exposure to hydrogen sulfide. A rate law is derived together with a tabulation of values of exponents and coefficients for the promoted ($\text{Ir/Ni/Al}_2\text{O}_3$) and the unpromoted ($\text{Ni/Al}_2\text{O}_3$) catalysts. Based on the rate law, the interaction of chemical kinetics and mass transport is analyzed in terms of the effect of catalyst pore size on the steady-state rate of methanation in a reaction of negative order with respect to CO.

The rate of deactivation of the catalyst by sulfur bearing feedstocks was evaluated in fixed bed reactors. Several types of reactor configuration were used in order to elucidate different aspects of catalyst performance. These aspects included the inherent deactivation

kinetics of the catalyst, long term performance, and catalyst behavior under conditions of constant conversion. The experimental results, in conjunction with a theoretical model, permitted evaluation of a poisoning coefficient that characterized catalyst deactivation in the absence of mass transfer limitations. Further, the data were also interpreted to give quantitative estimates of catalyst lifetime in bed geometries in which diffusional transport limited the rate of deactivation.

The performance of the Ir-promoted catalyst was examined also with respect to deactivation agents other than hydrogen sulfide. Ammonia as a feedstock contaminant up to the 1000 ppm level was found to have a negligibly small effect on methanation activity under the conditions of our tests. Under reactor conditions conducive to carbon deposition on nickel-on-alumina catalysts, the iridium-promoted catalyst exhibited a superior resistance to carbon fouling. Study of the combined water gas shift-methanation reaction indicated that the contribution of the water gas shift reaction was comparable for both catalysts.

In summary, the results of this study demonstrate that the Ir-promoted $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst possesses several valuable and superior characteristics when used for catalytic methanation under typical industrial conditions. These properties include:

- Higher activity by a factor of > 2 than that of the unpromoted $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst.
- Enhanced resistance to deactivation by hydrogen sulfide during exposure to contaminated feedstock, as manifested by the prolonged high methanation activity and extended service lifetime.
- High resistance to carbon fouling.

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I INTRODUCTION

The production of methane by catalytic reaction of carbon monoxide and hydrogen is an important process step in SNG production from coal. One of the process variables is the makeup of the catalyst and its performance characteristics in contact with the low-Btu gas mixture resulting from coal gasification and shift conversion. Ideally, a methanation catalyst should be able to operate with feedstocks obtained from so-called first generation gasification processes, such as Lurgi, operating at low pressures from (0.7 to 2 MPa), and from second generation plants, such as Synthane and Hygas, operating at pressures higher than 6.8 MPa. Among the transition metals, nickel-based catalysts are most suitable for methanation. However, they impose operating limitations in terms of purity of the syn gas because of their sensitivity to deactivation by feed gas contaminants and carbon deposits. A methanation catalyst with improved poisoning resistance would markedly increase the cost effectiveness of SNG production.

In our laboratory a catalyst was developed¹ that exhibits high methanation activity and notable sulfur poison tolerance. It contains nickel on an alumina support promoted with low concentrations of iridium (< 1 wt%).² Sulfur resistance of the catalyst was tested by exposure to CO/H₂ gas mixtures containing low concentrations of hydrogen sulfide. Experimental results from laboratory-scale experiments demonstrated (1) a catalyst half-life greater by a factor of three over that of a conventional methanation catalyst, (2) an increase in specific methanation activity greater by a factor of two, allowing reactor operation at considerably higher space velocities, and (3) resistance to sintering on exposure to high temperatures. These laboratory-scale studies pointed to further testing of the novel catalyst system under operating conditions and feedstock composition similar to those encountered in industrial methanation plants. Because the cost of removal of catalyst poisons from the feed gas increases markedly with the level of purity needed,

the development of a more poison-resistant catalyst provides considerable economic incentive.

In the current study, our objective was to conduct a bench-scale evaluation of the promoted methanation catalyst over a range of operating conditions encountered in industrial practice. This report describes in detail the experimental studies performed including evaluation of methanation kinetics with a gradientless internal recycle reactor, catalyst performance studies in the presence of feed gas impurities, and process design considerations for catalytic methanation.

II EVALUATION OF METHANATION KINETICS WITH A GRADIENTLESS INTERNAL RECYCLE REACTOR

To obtain information on the kinetics of methanation catalyzed by the promoted catalyst, we used an internal recycle reactor that operated under gradientless conditions (Berty reactor). The methanation kinetics were evaluated for the unpromoted $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst and the promoted $\text{Ir}/\text{Ni}/\text{Al}_2\text{O}_3$ catalyst over a range of temperatures (550 to 600 K) and pressures (up to 2.2 MPa).

A. Experimental Details

1. Catalysts

Of the two catalysts used in our kinetic measurements, one was a commercial nickel catalyst (G-65) with the following composition: 25 wt% Ni, 8 wt% alkali, 1 wt% graphite, and the balance alumina.* This material, in the form of 1/8-inch extruded pellets, was crushed and screened to a particle size range from 0.500 to 0.851 mm (20 to 32 Tyler mesh size). The other catalyst, an Ir-promoted material, was prepared by impregnating G-65 with a sufficient quantity of an aqueous solution containing K_2IrCl_6 to deposit 1.0 wt% iridium, and exposing it at room temperature to a solution of 5 wt% hydrazine in 0.5 N NaOH for reduction to the metallic phase. The sample was then washed in hot distilled water until no Cl^- ions were detectable, as monitored by exposure of an aliquot to the wash water to 1 M AgNO_3 . After drying, the catalyst was crushed and screened to 20/32 mesh. Additional details of the preparation of the Ir-promoted catalyst can be found in the patent literature for this catalyst.² Preceding the kinetic studies, each catalyst sample was reduced in situ in a stream of flowing hydrogen at 0.1 MPa and 723 K for at least 15 hours.

*Catalyst G-65 was provided by United Catalyst, Inc., Louisville, Kentucky 40232.

2. Apparatus

The experimental reactor system for kinetic studies (shown schematically in Figure 1) includes a compressor and high pressure reactor (Figure 2). The Berty autoclave (supplied by Autoclave Engineers and shown in detail in Figure 3) has been modified to accommodate small volumes (up to 5 cm^3) of powdered catalyst. Feed gas is introduced at the bottom of the reactor where it is immediately mixed and recirculated by an impeller; it then passes along the reactor walls and down through the draft tube and catalyst bed. The impeller, located just below the catalyst bed, can be operated at speeds from 50 to 2000 rpm to give a pressure drop for gas flow through the catalyst bed from 0.3 to 400 cm of fluid head. A high internal recycle ratio (≥ 50) ensures that the conversion rate per pass is below a specified $\pm 3\%$ limit and restricts the temperature rise through the bed to below 3 K. Thermowells, located 2 cm above and 0.5 cm below the catalyst bed, are used to record the thermal gradient through the bed. Since the original reactor thermocouples were mechanically stiff, electrically grounded, and fragile, we found it necessary to replace them with flexible 0.159 cm-OD thermowells and 0.079 cm flexible, ungrounded thermocouples (Omega Engineering, Inc). The reactor is heated by 3-KW heating elements contained in a shroud that surrounds the sides and top of the autoclave. A proportional controller (Leeds and Northrup) with $\pm 25\text{ K}$ bandwidth and 0.01 min^{-1} reset rate is capable of controlling the reactor temperature to $\pm 1\text{ K}$ by sensing the reactor temperature at several points along the wall of the autoclave. The heat released by the methanation experiments is small relative to the heat required to maintain the autoclave at the desired temperature (less than 10 W versus 750 W, respectively, at 600 K).

The volume, diameter, and particle size of the catalyst bed were chosen to minimize concentration and temperature gradients through the bed. The optimum particle size, roughly 0.05 cm, was determined by minimizing the resistance to internal recirculation (which increases with decreasing particle size) and the effect of pore diffusion (which increases with increasing particle size).

The feed gases are mixed and compressed when necessary at constant flow before entering the reactor. The reactor pressure can be adjusted up to 6.8 MPa with a back-pressure regulator (Tescom), which maintains the set pressure to within ± 0.02 MPa for a flow of up to $16.7 \text{ cm}^3/\text{sec}$. The gas composition is adjusted by calibrated flow-recording controllers (Tylan Corporation) on the CO and H_2 lines. These controllers measure and control the mass flow rate of each gas stream to within $\pm 2\%$, independent of pressure. The compressor (Aminco) is capable of compressing $15 \text{ cm}^3/\text{s}$ feed gas to 6.8 MPa at a suction pressure of 1 MPa. Surge tanks (250 cm^3) and a by-pass metering valve are used to dampen flow fluctuations and stabilize the suction pressure.

The carbon monoxide (Matheson, 99.99% purity) is purified by passage through a 13X molecular sieve trap maintained at 196 K. Hydrogen (Airco, 99.995% purity) is used as-received. The feed gas manifold also has ports for CH_4 or CO_2 and helium, which is used to flush the autoclave before reduction by hydrogen or reaction of synthesis gas. The helium (Liquid Carbonic, 99.995% purity) is purified by passage through a molecular sieve trap cooled with liquid nitrogen and is also used as the carrier gas in our gas chromatographic analysis.

Reactant and product gases are analyzed for H_2 , CO, CH_4 , CO_2 , C_2H_6 , and C_3H_8 with a gas chromatograph (Carle Instruments) that samples automatically at 960-second intervals. Inlet, outlet, or calibration gas mixtures can be selected for analysis by means of an 8-port switching valve (Valco). Water is removed from the product gas on the upstream side of the chromatograph inlet by condensation in a cold trap kept at 200 K.

The concentration of H_2O in the reactor effluent is calculated from the difference between CH_4 and CO_2 production rates, presuming an oxygen balance and noting that the levels of air and CO_2 in the feed gas are vanishingly small. Given the stoichiometry of the methanation and water gas shift reactions,

and

the concentration of CH_4 must equal the sum of the H_2O and CO_2 concentrations when CO is the sole source of oxygen; that is, the H_2O concentration must equal the difference in CH_4 and CO_2 concentrations.

3. Procedures

In a typical methanation experiment a 1-g sample of catalyst is placed in the reactor between two 40-mesh stainless screens in a very thin layer to minimize the flow resistance through the catalyst bed. After the reactor is sealed, it is pressurized to 50 psig in helium and checked for possible leaks. Then, with a H_2 flow of approximately 40 $\mu\text{mol/s}$ at 0.1 MPa pressure, the reaction is brought up to a temperature of 723 K for 15 hr. During the reduction, more than $50 \times 10^3 \text{ cm}^3$ of H_2 are passed through the reaction vessel.

The reactor temperature is controlled with a Leeds and Northrop controller that senses the reactor wall temperature. The temperature above the catalyst bed and the temperature difference through the bed are monitored with a strip-chart recorder. In addition, temperature readings are taken with a potentiometer at the time of GC sampling.

In the catalyst studies described below, the CO concentration in the reactant stream ranged from 2 to 22 vol% (balance H_2) at total gas pressures of 1, 5, and 21 atm and temperatures varying from 525 to 560 K. Typically, the flow of H_2 was held constant at about 8 cm^3/s (NTP) and that of CO was varied. The total gas flow to the reactor varied between 300 to 900 $\mu\text{moles/s}$, which is equivalent to a single-pass space velocity of the feed stream of approximately $4 \times 10^4 \text{ hr}^{-1}$.

The following procedure was used for the kinetic studies after catalyst reduction:

- (1) The desired reactor temperature was allowed to come to a steady-state condition during a 12- to 14-hr period.

- (2) Subsequently the impeller speed was increased from a "standby" of 500 rpm to 1500 rpm. The H_2 flow was increased from $0.7 \text{ cm}^3/\text{s}$ to $8 \text{ cm}^3/\text{s}$.
- (3) CO was introduced into the system at the lowest concentration level desired for this set of experiments.
- (4) For each specific CO flow rate, the feed-gas composition was determined both before and after analysis of the product gas. A period of approximately 1-3 hr was required to reach steady-state operation after a change in CO feed concentration. Temperatures were monitored each time a change was made in the feed gas composition and recorded when samples were taken for analysis.
- (5) At the end of a run, the CO was turned off and the impeller speed and H_2 flow rate were lowered to standby values.

The independently controlled experimental variables are the total feed rate, feed composition, reaction temperature and pressure, catalyst volume, and particle size. The catalyst volume and particle size were chosen to minimize inter- and intra-particle mass transport gradients. The reaction temperature and total pressure were held constant during an experiment, leaving the reaction kinetics to be studied as a function of H_2/CO feed ratio, CO feed rate, and time. The reaction was considered to be at steady-state conditions after passing 3 reactor volumes of feed gas for a given feed rate and composition and after at least 100 molecules of CO were converted for each surface atom of the metal catalyst (defined by CO or H_2 chemisorption on freshly reduced catalyst). Generally an hour or less was required to reach steady state although up to 3 hr were required at 2.1 MPa total pressure with high CO concentration or with low temperature.

For investigation of the reaction kinetics with partially poisoned catalysts, samples were used that had been presulfided in a recirculating reactor by exposure to sulfur compounds. First, each catalyst sample (1 g each) was reduced in H_2 for 1 hr at 723 K. Then 100 μmol of sulfur was injected as a mixture of H_2S and He into the recirculating system.

After 16 hr in the recirculating system, the samples were cooled in He, transferred to the Bertly reactor, and again reduced at H_2 under conditions identical to those used with unsulfided catalyst. Methanation activity for these sulfur-poisoned catalysts was measured under gradientless conditions at a total pressure of 0.1 MPa.

B. Experimental Results

1. Reaction Kinetics at Atmospheric Pressure

The methanation activities of the Ir-promoted and unpromoted Ni/Al_2O_3 catalysts after exposure to H_2S/H_2 were studied first at a total pressure of 1 atm (1.03×10^5 Pa) with sulfur-free synthesis gas. The H_2/CO feed ratio varied from 43 to 3.6 with bed temperatures from 523 to 556 K for the unpoisoned catalysts and 516 to 606 K for the sulfur-poisoned catalysts.

The rates of methane formation of the unpoisoned catalysts exhibit a maximum with increasing CO concentration in the recirculating reactor (Figures 4 and 5). The decrease in conversion is caused by CO inhibition of the reaction rate as observed previously.³ At low mole fractions of CO ($X_{CO} < .02$), however, the methanation rates show first-order dependence on CO and little dependence on temperature. We interpret this behavior to be caused by diffusion-limited reaction. The actual bed temperatures were corrected by adding 0.35 K per $\mu\text{mol/s}$ methanation rate to the measured upstream gas temperature. Such a correction was necessary because the low internal recirculation flow velocity at 10^5 Pa H_2 is not sufficient to prevent a small temperature rise within the catalyst bed at high rates due to the highly exothermic nature of the reaction.

In the first order (low X_{CO}) regime, the differences in methanation rate between the Ir-promoted and the unpromoted catalyst are small despite the greater intrinsic activity rate of the promoted catalyst. Both catalysts have nearly the same physical properties, including pore diffusivities. Thus, the methanation rates over the two catalysts converge toward a common value under condition where diffusional mass transport governs the reaction kinetics.

The results of the methanation studies with H₂S-exposed Ni/Al₂O₃ and Ni/Ir/Al₂O₃ (Figures 6 and 7) exhibit reaction kinetics similar to that observed for the unpoisoned catalyst samples. Regression analysis was applied (Table 1) to the data for which the partial pressure of CO was sufficiently high that transport limitations were insignificant. The rate data was analyzed according to the empirical rate law

$$R_{CH_4} = k \cdot P_{CO}^y \text{ mol} \cdot g^{-1} \cdot s^{-1} \quad (3)$$

where k represents the rate constant and y the power law exponent for the partial pressure P of CO (in atmospheres). Because of the relatively small variation in the partial pressure of H₂ during these experiments, we did not include it explicitly in the rate equation. The outlet H₂ concentration varied only from 75 vol% to 95 vol%. Over the temperature range from 525 to 559 K with $P_{CO} > 1 \times 10^4$ Pa, the methanation-rate ratio between Ir/Ni/Al₂O₃ and Ni/Al₂O₃ varied from 1.5 to 2.1, normalized by CO adsorption capacity at 300 K. The activation energies derived from these data (Table 1) are nearly the same, within experimental error. The higher activation energy of the sulfur-free Ni/Al₂O₃ catalyst, although statistically significant, is based on a narrow temperature range (10 K) and may be in error by $\pm 10\%$. The least-squares activation energy for fresh Ni/Al₂O₃, 159 kJ/mol, is higher than reported for supported nickel³ (~130 kJ/mol). In addition, the ME rate for all catalysts was proportional to $P_{CO}^{-0.43 \pm 0.04}$.

Although the activity of both catalysts declines on exposure to sulfur, the methanation activity of the Ir-promoted catalyst was much less affected by the sulfur poison than the unpromoted catalyst. Relative to Ni/Al₂O₃ we find that the iridium-promoted catalyst has three times the methanation activity per unit weight of catalyst after exposure to the same dose of H₂S. On the other hand, the activity of the freshly reduced sulfur-free Ni/Ir/Al₂O₃ catalyst was 50 to 110% greater than that of Ni/Al₂O₃.

2. Reaction Kinetics at Elevated Pressures

In our studies of the steady-state methanation rates catalyzed by $\text{Ni}/\text{Al}_2\text{O}_3$ and $\text{Ni}/\text{Ir}/\text{Al}_2\text{O}_3$ under gradientless conditions and at total pressures ranging from 0.53 to 2.2 MPa, the product composition was monitored as the feed gas progressively displaced the initial volume of hydrogen. Again, as observed at low pressures, the results (Figures 8 and 9) indicate that with increasing CO levels in the reactor, the rate of methane formation goes through a maximum. Steady state was quickly reached at low CO partial pressure. However, for P_{CO} above ~ 0.03 MPa, a continuous slow decline in methane concentration was observed for periods up to 5 hr. This effect was reversible because a decrease in CO feed concentration caused a slow recovery of the CH_4 production rate.

Hydrogen partial pressure had little influence on the ME rate relative to CO. At constant CO partial pressure and temperature, we estimate that the reaction order of the ME rate with respect to H_2 partial pressure is 0.2 ± 0.1 . The reaction order with respect to other gas phase components was not analyzed, but previous work³ has shown that CO_2 , H_2O , and CH_4 have little effect; also, the gas composition is far from equilibrium in our studies.

The selectivity for methane was substantially reduced at higher total pressures and especially with high CO partial pressure ($> 3.1 \times 10^4$ Pa). In Figures 10 and 11 we show the rate of C_2H_6 production for the two types of catalysts studied. Linear regression analysis was performed on the C_2H_6 formation rates (Table 2). In contrast to CO inhibition of the methanation rate, the rate of ethane production is nearly first order in CO pressure. The rate of C_2H_6 production was not substantially influenced by temperature over the narrow range used in our studies, nor did hydrogen pressure (0.45 ± 0.05 to 1.80 ± 0.25 MPa) appreciably alter the C_2H_6 formation rate. Also, within experimental error, the C_2H_6 formation rate was the same for both catalysts.

We were unable to detect small concentrations of higher molecular weight hydrocarbons. The dry-ice-cooled molecular-sieve trap,

used to remove water vapor from the gas sample before admittance to the GC system, will trap C_5^+ hydrocarbons. Also the GC system, as currently set up, detects C_3^+ hydrocarbons along with untrapped water vapor without separation. Therefore, it was difficult to estimate the product yield for C_3^+ hydrocarbons. On the basis of a carbon balance, we estimate their concentration to be less than 5 wt%.

C. Analysis of Reaction Kinetics and Methanation Mechanism

1. Effect of Carbon Monoxide

The kinetic data at 0.1 MPa total pressure for the sulfur-free Ni/Al₂O₃ catalyst provide not only a basis for comparison with the activity of Ni/Ir/Al₂O₃ and with the sulfur-poisoned catalysts, but also for comparing the results of our study with previous work.

Published data³ for supported nickel catalysts list apparent activation energies ranging from 73 to 130 kJ·mol⁻¹, and reaction orders for CO partial pressure varying from -0.2 to -0.9. Specific activities per surface Ni atom (turnover numbers) have been tabulated³ for methanation by supported nickel catalysts at 548 K in 0.025 MPa CO and 0.075 MPa H₂. The turnover numbers (N) under these conditions ranged from 0.035 to 0.099 s⁻¹ with a mean value of 0.07 s⁻¹. Our specific methanation rates at 548 K yield $N = 0.085 \text{ s}^{-1}$.

The complex dependence of the rates on P_{CO} and the possibility that pore diffusion within the catalyst particles may limit the observed reaction rates complicate the interpretation of the rate data in terms of a mechanistic model. However, we have developed a relatively simple methanation mechanism that adequately describes the observed dependence of the rate on P_{CO} . This model draws on fundamental studies of the interaction of CO with nickel surfaces as reported in the literature, including work performed in this laboratory. Using this model, we are able to determine the influence of pore diffusion in the observed rates by computing the effectiveness factor as a function of effective diffusivity, particle size, P_{CO} , and the methanation rate in the absence of diffusional limitations.

The kinetics of methanation on nickel is dominated by CO inhibition. Our results show that for partial pressures of CO higher than 0.01 ± 0.005 MPa, the rate of methanation decreases approximately as $P_{CO}^{-1/2}$; on the other hand, as P_{CO} approaches zero, the reaction must become proportional to P_{CO} . Concerning the reaction mechanism, recent evidence⁴⁻⁷ points toward dissociation of adsorbed CO without direct H_2 participation as the first step in methanation on metals. CO inhibition then would be viewed as a result of competition of CO for vacant sites required for CO dissociation. We can construct a model of methanation based on site competition. Let us consider the methanation rate to be governed by

$$R_{CH_4} = k_d \theta_{CO} \theta_s \quad (4)$$

where θ_{CO} is the fractional CO coverage, θ_s is the vacant-site fraction, and k_d is the rate constant for dissociative chemisorption of CO.

Assuming that two adjacent sites are occupied by CO, the number of unoccupied sites is given by

$$\theta_s = 1 - 2\theta_{CO} \quad (5)$$

In addition, for the adsorption equilibrium of CO, we write

$$\theta_{CO} = K_e P_{CO} \theta_s^2 \quad (6)$$

where K_e represents the equilibrium constant for the sorption step. By combining equations (5) and (6), we obtain

$$\theta_s = (\sqrt{1 + 8K_e P_{CO}} - 1) / 4K_e P_{CO} \quad (7)$$

which, when introduced into equation (4), yields

$$R_{CH_4} = k_d (\sqrt{1 + 8K_e P_{CO}} - 1)^3 / 64K_e^2 P_{CO}^2 \quad (8)$$

One can readily show that as $P_{CO} \rightarrow 0$, $\text{Rate} \rightarrow k_d K_e P_{CO}$, and that as $P_{CO} \rightarrow \infty$, $\text{Rate} \rightarrow k_d (8K_e P_{CO})^{-1/2}$ with maximum rate $(k_d/8)$ at $P_{CO} = K_e^{-1}$. From published data for CO chemisorption on nickel,⁸⁻¹² we find an average value for K_e to be $2.0 \times 10^{-9} \exp(13340/T)$. The predicted rate is very sensitive to the value of k_d , a value that is not precisely known. The dissociation rate constant is estimated to be $k_d = 1.0 \times 10^{12} \exp(-14570/T) \text{ s}^{-1}$ based on CO dissociation^{13,14} and disproportionation rates^{4,6,7,10,14,15} at 423 K in the absence of hydrogen. The activation energy for k_d was chosen to give $1/k_d = 900 \text{ s}$ at 423 K with a reasonable surface dissociation frequency factor, $1.0 \times 10^{12} \text{ s}^{-1}$. By substituting into equation (4) at 540 K and a total pressure of 0.1 MPa, we can calculate the maximum ME rates and P_{CO} at maximum rate for the nickel and the Ir-promoted nickel catalysts.

Catalyst	P_{CO} MPa at Maximum Rate		Maximum Rate ($\mu\text{mol/g}\cdot\text{s}$)	
	Calculated	Experimental	Calculated	Experimental
Ni/ Al_2O_3	0.00093	0.0021	15	11
Ni/Ir/ Al_2O_3	0.00093	0.0025	23	19

The maximum ME rates predicted by the model are greater than the observed rates and the maximum rate occurs at higher P_{CO} than predicted. Limiting pore diffusion of reactant CO probably causes the slower observed rates at the predicted maximum point.

Pore diffusion is generally expected to restrict the reaction rate. Slow diffusion causes the reactant concentration to decrease within the interior of a catalyst particle. For a first-order reaction, the rate declines within the interior. But in the case of a catalytic reaction inhibited by a reactant, just the opposite effect may result. Since the rate exhibits a negative reaction order, the rate actually increases as the reactant concentration decreases within the particle. Thus the volume-averaged reaction rate can be greater for slow pore diffusion than for very fast diffusional transport. As $P_{CO} \rightarrow 0$, we know the reaction rate must ultimately become proportional to P_{CO} , as

described by the CO site-competition model. If pore diffusion is very restrictive, the concentration gradient becomes very steep near the surface and P_{CO} and the local reaction rate both become very low within the interior of a particle. The volume average rate can then decline to a value well below the rate expected if restrictive pore diffusion was absent.

2. Effect of Hydrogen

The simple CO inhibition model, although adequate for relating the effectiveness factor to the methane formation rate, does not account for the effect of H_2 partial pressure on the methanation kinetics. The model as described above attributes the methanation rate solely to CO dissociation, inhibited by site-competition with chemisorbed CO. Hydrogen was assumed to react rapidly with both C and O adspecies following CO dissociation. Although reaction of H_2 with adsorbed oxygen may be very rapid,¹⁶ reaction of H_2 with chemisorbed carbon may not be substantially faster than CO dissociation above 525 K.¹⁷ Therefore, we must extend the site-competition model to include chemisorbed, reactive carbon as well as adsorbed CO. Hydrogen would then influence the rate of removing carbon, thus freeing reactive sites for additional reaction.

We express the rate of methane production as

$$R_{CH_4} = k_h \theta_c P_{H_2}^{0.5} \quad (9)$$

where θ_c is the fractional coverage with carbon atoms and k_h is a rate constant. The actual pressure dependence of the rate of hydrogenation on chemisorbed carbon is uncertain. Work in our laboratory has shown less than first-order dependence on P_{H_2} .¹⁷ Half-order dependence suggests the rate is proportional to the hydrogen atom population on the catalytic surface. From a carbon balance at steady state, we must have

$$k_h \theta_c P_{H_2}^{0.5} = k_d \theta_{CO} \theta_s, \quad (10)$$

so that the rate of chemisorbed carbon formation equals the hydrogenation rate. Assuming that both CO and carbon occupy two adjacent sites, the number of unoccupied sites is given by

$$\theta_s = 1 - 2\theta_{CO} = 2\theta_c \quad (11)$$

Expressing CO adsorption as in equation (4), we have

$$2 \left(k_d K_e P_{CO} / k_h P_{H_2}^{0.5} \right) \theta_s^3 + 2K_e P_{CO} \theta_s^2 + \theta_s - 1 = 0 \quad (12)$$

and

$$R_{CH_4} = k_d K_e P_{CO} \theta_s^3 \quad (13)$$

Equation (12) defines θ_s as a function of T , P_{CO} , and P_{H_2} , and substitution in equation (13) gives the rate. The available literature values for the reaction of hydrogen with chemisorbed reactive carbon^{7,17} are restricted to H_2 pressures below 1 atm. Previous work in our laboratory¹⁷ has shown that $k_h = 2.0 \times 10^6 \exp(-8550/T)$ for $P_{H_2} = 0.1$ MPa. The rate of hydrogenation decreased by a factor of 5 for $P_{H_2}^2 = 0.001$ MPa, which indicates a reaction order of 0.35.

The ME rate data have been analyzed with the kinetic model represented by equations (12) and (13). First the effect of diffusion was removed by estimating the effectiveness factor (see Section IV.A) and correcting the observed rate to give the rate expected in the absence of gradients due to pore diffusion. Given experimental values of P_{CO} , P_{H_2} , and temperature, we determined the values of E_d , the activation energy for CO dissociation, which gave the corrected experimental ME rate as the solution to equations (12) and (13). Thus only a single parameter, E_d , was used to fit the observed and corrected rate data to the site competition model for both catalysts. All values for E_d fell within ± 3.5 kJ/mol of the anticipated value for CO dissociation $E_d = 121.1$ kJ/mol (as discussed above).

Preliminary conclusions can be drawn from this analysis of the ME rate data. The small variance of the fitted values for E_d shows that

the model predicts the ME rate reasonably well. The fact that most variables in the model were estimated from separate studies supports the plausibility of the site competition—CO dissociation model. The rate is limited by diffusion for low P_{CO} (illustrated for the Ni/Ir/Al₂O₃ catalyst at 550 K and 2.1 MPa total pressure (Figure 12)). Also, the model suggests that appreciable carbon must cover the catalyst surface if P_{H_2} is to have any influence on the ME rate. The predicted influence of P_{H_2} on the overall rate is less than 0.35, which is in agreement with our observations.

3. Effect of Surface Sulfur on Catalytic Activity

The experiments with the sulfided catalysts demonstrate the enhanced sulfur tolerance of the Ir-promoted nickel catalyst. The fact that the activation energies for both catalysts remain unaltered within experimental error by sulfur poisoning suggests that the catalytic mechanism is unchanged. The superior sulfur tolerance of the Ir-promoted catalyst is apparently due to its ability to retain a relatively greater number of active sites when exposed to equal amounts of sulfur. This may be the result of (1) a greater initial site density of the Ni/Ir/Al₂O₃ catalyst, (2) a change in the coordination number for sulfur adsorption, and (3) a change in binding energy of sulfur. These effects remain to be established.

III. CATALYST PERFORMANCE STUDIES WITH FIXED BED REACTORS IN THE PRESENCE OF FEED GAS CONTAMINANTS

For performance evaluation of the promoted catalysts in the presence of feed-gas contaminants, we selected fixed bed reactors. Several types of reactor configuration and variations in process conditions were used so as to elucidate different aspects of catalyst performance.

In the first series of experiments, designed for the analysis of poisoning kinetics, we used small reactors and operated at high space velocities. Subsequently, we measured catalyst performance under conditions approximating an adiabatic reactor adjusted to operate continuously at constant reactant conversion, analogous to an industrial methanator. Long-term measurements of catalyst performance under conditions of high conversion rate were performed in a third set of experiments using larger fixed bed reactors.

In each series, two reactors were used with identical catalyst charges, except that one was loaded with 25 wt% Ni/ Al_2O_3 whereas the other was loaded with 1 wt% Ir/25 wt% Ni/ Al_2O_3 . Identical feed gas and reaction conditions were selected to ensure an accurate comparison of performance of the respective catalysts. The reactor characteristics and conditions used in these experiments are summarized in Table 3.

A. Experimental Details

1. Apparatus

In the fixed bed reactor studies, the same gas supply and gas-analysis procedures (Figure 13) were used as with the gradientless internal recycle reactor (Section II). The stainless steel reactors were fabricated from Type 304 tubing or pipe, with a fine-mesh screen welded in place to support the catalyst bed. Dimensions and geometric configurations for the different reactors used in the study are listed in Table 3 and shown in Figure 14. Microreactors were made from Pyrex

tubing, using a glass frit to support the catalyst.

Each reactor was heated with external electrical furnaces; its temperature was maintained at the desired level by temperature controllers. The heaters for the larger reactors were composed of segmented electrical resistance elements that permitted adjustment of the heat input to provide a uniform axial temperature profile (± 5 K) in the absence of reactant in the feedstock.

Gas flow rates into the reactors were metered with calibrated electronic flow controllers (Tylan Corporation). The total gas pressure in the reactors was controlled by a Tescom backpressure regulator situated at the reactor outlet (Figure 13).

2. Catalysts

The two catalysts used in this portion of the study consisted of a commercial catalyst^{*} with 25 wt% nickel on an alumina support, and an iridium-promoted catalyst prepared in this laboratory, containing 1 wt% Ir and 25 wt% Ni on alumina support. (Details of catalyst preparation procedures are given in Section II.A.) For some of the present tests, where it was desirable to extend the size of the active bed and to dissipate the exothermic heat of reaction associated with methanation, the catalysts were uniformly diluted with α -alumina[†] of low surface area.

The beds of the promoted and the unpromoted nickel catalysts were identical in all respects except for catalyst composition. Before tests were begun, both catalysts were reduced and activated in situ in a stream of hydrogen at 0.1 MPa and 673 K for at least 15 to 37 hr. Subsequently, the temperature was reduced to the desired level and the feed gas was allowed to replace the hydrogen.

^{*}This catalyst--manufactured by United Catalysts, Louisville, Kentucky--carries the designation G-65.

[†]Manufactured by Kaiser Aluminum and Chemical Corporation (Surface Area = $20 \text{ m}^2 \cdot \text{g}^{-1}$).

3. Feedstock

Premixed synthesis gas (syn gas), supplied in aluminum cylinders by Scientific Gas Products, Inc., was used as a feedstock for the tests. The syn gas contained 25 mol% CO, 75 mol% H₂ (H₂/CO = 3.0 ± 0.1), and, nominally, 10 ppm H₂S. (The actual H₂S content of the syn gas varied from tank to tank, as determined by our feedstream analyses.) To simulate product gas recycle through the fixed bed reactors, we dilute the syn gas with an inert gas (high purity nitrogen 99,995%), before it entered the reactor. Hence, the feedstock contained H₂S at a reduced level in inverse proportion to the dilution ratio (Table 3).

4. Analytical Methods

Sampling of gas from the common feedstream and from the product streams of the individual reactors could be selected by means of a multi-port switching valve (Figure 13). Samples were taken automatically at specified time intervals and analyzed for H₂, CO, CH₄, CO₂, C₂H₆, and C₃H₈ by means of a Carle Series-S AGC gas chromatograph. The concentration of water in the reactor effluent was determined on the basis of an oxygen balance.

Analysis for H₂S was performed with an HNU photoionization detector on separate gas samples passed through a chromosil column (165 cm in length, 0.32 cm in diameter). With this system we could detect H₂S at concentrations as low as 2 ppb. The compositions of both the feedstream and the product streams were monitored at frequent intervals.

To determine whether the feedstock H₂S was being converted to COS in the reactors, we analyzed a number of gas samples in a separate chromatograph equipped with a Tracor flame photometric sulfur detector. The H₂S levels observed were comparable to those obtained with the photoionization detector, but only trace amounts of COS were detected.

B. Experimental Results on Catalyst Deactivation

Three types of experimental measurements were used to monitor the process of catalyst deactivation by H₂S in the feed gas. In the first procedure, the changes in the fractional conversion to methane at constant

feed-gas composition were monitored to determine the decay in catalyst activity with exposure. In the second procedure, the fractional conversion to methane was maintained at a constant level during catalyst deactivation by continuous adjustment of the space velocity. This decrease in the volumetric flow rate of feedstock was a quantitative measure of the rate of loss of activity. The third procedure involved measurement of the progressive movement of the reaction zone through the catalyst bed under conditions of high fractional conversion, as reflected by changes in the axial temperature profile in the catalyst column. The results of each of these experimental procedures are discussed below.

1. Experiments with Fixed Inlet Conditions to Reactor

Experiments were performed in small Pyrex reactors to obtain the kinetic parameters for methanation and catalyst deactivation in the fixed bed reactors, and to clarify the potential contribution of internal or external mass transport processes on the distribution of sulfur through the catalyst bed. In these experiments, 0.03 g of the catalyst (170-250 mesh, 61-88 μm particles) was loaded into a glass microreactor provided with a glass frit to hold the catalyst bed. The reactor pressure was 8.8 psig (1.58×10^5 Pa), the space velocity was 194 s^{-1} ($7 \times 10^5 \text{ hr}^{-1}$), and temperature was 540 K, as measured by a thermocouple on the reactor wall.

The methanation-activity patterns of the Ir-promoted and unpromoted $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst demonstrated significant differences (Figure 15). The initial activity of $\text{Ir}/\text{Ni}/\text{Al}_2\text{O}_3$ was found to be considerably higher and its rate of deactivation by the H_2S -containing syn gas was markedly lower than the values obtained for the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst.

2. Experiments with Constant Conversion

In industrial practice, reactors are operated under adiabatic conditions with the inlet parameters continuously adjusted to give a constant yield of product. We simulated such conditions in a bench-scale fixed bed reactor using the two catalysts of interest.

In these measurements, feedstock with a constant concentration of H_2 , CO , and H_2S was diluted by admixture of N_2 to simulate the feed

at the inlet to a fixed bed, external recycle reactor. The catalyst beds were prepared by uniformly dispersing a small mass of active catalyst in a matrix of alpha alumina particles of the same size distribution (Table 3). The use of such a bed permitted the attainment of feedstock space velocities comparable to industrial practice, and reduced the time required to observe a significant loss of activity due to poisoning. The inlet temperature of the gas and the total pressure in the reactor were maintained constant by appropriate control devices. The fractional conversion of the CO to methane was monitored by analyses of the feed and product streams. As the activity of the bed diminished because of the action of the feedstock H_2S , the space velocity of the feedstock was reduced to keep the fractional conversion constant. This change in space velocity with time at constant conversion is a measure of the decay of the catalyst under the imposed conditions. The results of these experiments provide a direct comparison in productive lifetimes between beds of the two catalysts for a given yield of product. Experiments with the Ir-promoted and the unpromoted catalysts were performed sequentially. Initial space velocities were adjusted to give the desired fractional conversions for the two catalysts (Table 3).

The results obtained from these measurements are summarized in Figures 16 and 17. For any given exposure to feed gas, the ratio of space velocities is nearly the same as the ratio of methane conversions, indicating that kinetic control prevails and that the catalytic reaction is not transport-limited. Furthermore, the data exhibit the large difference in methanation activity of the two catalysts, as reflected in their respective space velocities for constant methane yield.

3. Long-Term, High Conversion Experiments

In a fixed bed reactor in which an exothermic reaction is occurring, the axial movement of the temperature maximum through the catalyst bed indicates the progressive poisoning due to feedstock contaminant. The rate of change of the axial temperature profile in the reactor is a measure of the global deactivation rate of the catalyst. We have used this type of experiment to evaluate the performance of the

two catalysts when exposed to H_2S -containing feedstock for relatively long periods of time (> 30 days).

To permit long-term operation, considerably larger catalyst beds were used than in the previous experiments (Table 3). Axial temperature profiles were interpolated from measurements of temperatures at four points within the catalyst bed (Figure 14). Experiments were performed in separate, parallel reactors sharing a common feed stream. Values of the experimental parameters are summarized in Table 3.

Typical temperature distributions in the respective catalyst beds after different periods of exposure to the H_2S -contaminated feedstock are shown in Figure 18. The rate of advance of the temperature maximum was significantly slower for the $1\text{Ir}/25\text{Ni}/\text{Al}_2\text{O}_3$ catalyst than for $25\text{Ni}/\text{Al}_2\text{O}_3$.

In addition to the temperature measurements, analyses of the product streams from both reactors were made at intervals during the experiment. As shown in Figure 19, the conversion of CO to CH_4 was complete for both catalysts for a period of several hundred hours. However, in the case of the unpromoted catalyst, a significant decline in conversion became noticeable after about 400 hr of operation. For the Ir-promoted catalyst, no decrease in total conversion is observed for as long as 650 hr. In each case, the decline in methane production was accompanied by the appearance of unreacted feed gas in the product stream. Methane synthesis ceased completely when the temperature maximum completed its traverse through the respective catalyst beds.

4. Surface Chemical Composition

After long-term exposure to H_2S -containing feed gas, catalyst samples were withdrawn from the top and bottom portions of the catalyst beds in the integral reactors and their surface composition was examined by Auger electron spectroscopy (AES). For these measurements the catalyst particles were mounted on coupons of indium foil and the Auger electron spectra were obtained with a Varian cylindrical mirror analyzer.

The following Auger electron transitions were used in the elemental analysis.

<u>Element</u>	<u>Auger Electron Transition</u>	<u>Energy (eV)</u>
Ni	$L_3M_{4,5}M_{4,5}$	840
Al	KL_2L_2	1400
O	KL_2L_2	510
S	$L_3M_{2,3}M_{2,3}$	150

To a good approximation, the amplitude of the observed Auger peaks are proportional to the concentrations of the respective components,¹⁸ and the peak height ratios are measures of the relative abundance of the respective components. However, to compensate for differences in Auger electron yield for the different peaks, it is necessary to apply a correction to each observed peak height based on standard peak heights obtained for pure materials under identical instrumental conditions.¹⁹ We have made such a correction in our data, which is summarized in Table 4.

As expected, the top portions of the two catalyst beds exhibit a much higher S/Ni than the bottom portions. In addition, the S/Ni for Ir/Ni/Al₂O₃ is smaller than that for Ni/Al₂O₃, indicative of a lower average surface density of sulfur on the Ir-promoted nickel surface. Elemental Ir was not detectable by AES under our experimental conditions. This result suggests that at the low weight loadings used in our study, the Ir was highly dispersed. At higher Ir weight loading, the formation of bulk alloys of Ir/Ni accompanied by surface segregation of Ir has been observed.²⁰

5. Effect of Ammonia

We examined the effect of ammonia on catalyst performance because it is a common impurity in syn gas produced by coal gasification, and because it adsorbs on iridium and tends to form a surface nitride at

about 600 K.²¹ Consequently, it is important to evaluate the effect of feedstock ammonia on the activity and lifetime of the iridium-promoted nickel-on-alumina methanation catalyst. For this purpose we made comparative measurements of the methanation activity of the iridium-promoted catalyst and the unpromoted catalyst exposed to ammonia-containing feedstock.

In these measurements, the catalysts were uniformly diluted with α -Al₂O₃ particles and loaded into fixed bed reactors. The syn gas (H₂/CO = 3) contained 1 vol% ammonia. The reactor pressure and inlet temperature were regulated at 50 psig and 530 K, respectively, and the space velocity was maintained at $3 \times 10^5 \text{ hr}^{-1}$ (Table 3).

As shown in Figure 20, both catalysts exhibit a small and identical decline in activity with exposure. There is no evidence that the iridium-containing catalyst is preferentially deactivated by the ammonia-contaminated feedstock. Consequently, we conclude that ammonia exhibits no special threat to the promoted catalyst under methanation conditions.

6. Carbon Deposition and Reactivity

The fouling of Ni-based methanation catalysts resulting from carbon deposits is a well-known cause of catalyst deactivation. This process of carbon deposition is likely to occur under conditions of temperature "spiking". Such temperature excursions result in sintering of the metal crystallites and formation of surface carbon.

Since the methanation reaction involves dissociative chemisorption of CO, the surface carbon species so formed is the precursor for methane formation as well as carbon fouling. The conditions favoring one process over the other are the surface carbon density and the catalyst temperature.¹⁷

Therefore, it is of interest to examine the carbon fouling tendencies of the two catalysts under study. To measure this surface property, we deposited carbon species on Ni/Al₂O₃ and Ir/Ni/Al₂O₃ by

exposing each catalyst to pulses of carbon monoxide that formed surface carbon (C_s) by the Boudouard reaction ($2CO \rightarrow C_s + CO_2$). Subsequently, we measured the rate of transformation of the labile surface carbon to methane by reaction with flowing H_2 while the temperature of the catalyst was raised at a prescribed linear rate. This technique of temperature programmed surface reaction (TPSR) and its application to the measurement of surface carbon reactivities has been described previously.¹⁷ Because of the labile nature of the surface carbon so formed, a number of carbon states can be identified by TPSR, as determined by the rate of methane formation over a range of temperature. A highly reactive carbon will form CH_4 at relatively low temperatures, whereas a nonreactive carbon deposit will require higher temperatures.

During the TPSR experiments, significant differences were observed with the two catalysts under study (Figure 21). On Ni/Al_2O_3 two prominent carbon states were noted, C_α and C_β . The C_α -state is of higher reactivity toward H_2 than the C_β -state. On $Ir/Ni/Al_2O_3$ the surface carbon is almost exclusively in the highly reactive C_α -state. As a result, the coking tendency of this catalyst under methanation conditions (less than 575 K) would be expected to be very much lower than that of Ni/Al_2O_3 .

7. Shift Conversion and Methanation

Earlier studies²² in our laboratory demonstrated that Ni/Al_2O_3 catalysts possess significant activity for the water gas shift reaction, particularly at temperatures greater than 625 K. In principle, therefore, it would be possible to use such catalysts for a shift/methanation process with syn gas containing $H_2/CO < 3$. However, on nickel catalysts, H_2/CO ratios less than about 2.6 tend to deposit carbon resulting in loss of activity because of fouling.²³

The Ir-promoted Ni/Al_2O_3 catalyst is more resistant to carbon deposition than an unpromoted catalyst (as shown in the preceding Section III.B.6). Consequently, it is of interest to evaluate the performance of the promoted catalyst for shift/methanation by examining the

yields of CH_4 and CO_2 with less than stoichiometric levels of feedstock H_2/CO ratios, and with steam added to the feedstock. To enhance the potential role of the shift reaction in methanation, we carried out our measurements at 723 K.

For these experiments we used a Pyrex microreactor containing a small mass of catalyst. CO and H_2 were metered through flowmeters, and then diluted with He before flowing into the reactor. Steam was added to the H_2 - CO feed by diverting the He stream through a water-filled bubbler maintained at constant temperature. All gas lines and valves were lagged with heating tape to prevent condensation of the steam. For analysis, samples of feedstock and of the product stream were injected directly into a gas chromatograph by means of multiport sampling vales.

The experimental results show little difference between the two catalysts in the contribution of the water gas shift reaction to the methanation process, as evidenced by nearly identical CO_2/CH_4 ratios for the two cases (Table 5). Also, the addition of H_2O to the feedstock causes little change in the measured CO_2/CH_4 ratio. These observations indicate that the promoted and the unpromoted catalysts possess similar activity for water gas shift.

For the promoted catalyst the carbon balance indicates the absence of carbon deposition over period of 15 hr at 523 K with a feedstock H_2/CO ratio as low as 1.6 in the presence of steam. This observation is in good agreement with our carbon deposition and reactivity studies using TPSR (Section III.B.6).

C. Theoretical Model for Catalyst Deactivation

In the following analysis we consider the passage of a gas mixture containing reactants and contaminants through a bed made up of catalyst particles. The average gas flow is nearly uniform at velocity V (or space velocity $U = V/L$, where L is the bed depth) so that variables, such as the local concentration n of contaminant species, are uniform over each cross section and are functions only of the distance x into the bed and the time t . The rate of catalyst deactivation by the contaminant

in the feed stream is taken to be of first order in n and in the number density s of active sites. The differential equation for convective transport of the contaminant species through the catalyst reads

$$\frac{\partial n}{\partial t} + V \frac{\partial n}{\partial x} = k_p n s \quad (14)$$

where k_p is the rate constant for catalyst deactivation.

The poisoning process is considered to involve a gaseous contaminant species that is irreversibly adsorbed so that the catalytic site density is reduced at the rate

$$\frac{\partial s}{\partial t} = -k_p n s \quad (15)$$

Although the differential system is nonlinear, a general solution has been obtained¹ in the form:

$$n = n_0 \theta / (\theta + \xi - 1) \quad (16)$$

$$s = s_0 \xi / (\theta + \xi - 1) \quad (17)$$

where

$$\theta = \exp\{k_p n_0 [t - (x/V)]\}$$

$$\xi = \exp(k_p s_0 x/V)$$

Here s_0 is the initial site density in the catalyst and n_0 is the gaseous contaminant density at the inlet to the catalyst bed.

For dilute feedstocks the methanation rates for the catalysts under study were found to follow the general rate law $R_{ME} \propto (a/b)^{1/2}$, where a and b represent the concentrations of hydrogen and carbon monoxide (see Section II). On the assumption that the same metal surface sites active for methanation are acceptor sites for the catalyst poison, one obtains for the convective transport of reactant species:

$$-\left(\frac{\partial a}{\partial t} + v \frac{\partial a}{\partial x}\right) = -\left(\frac{\partial b}{\partial t} + v \frac{\partial b}{\partial x}\right) = k_c s(a/b)^{1/2} \quad (18)$$

where k_c is the rate constant for methanation. Change of the independent variables from x and t to θ and ξ leads to

$$\frac{\partial a}{\partial \xi} = \frac{\partial b}{\partial \xi} = \frac{-k_c \sqrt{a/b}}{k_p (\theta + \xi - 1)} \quad (19)$$

so that

$$a = b + c(\theta) \quad (20)$$

where c is a function of θ only. The reactants have constant concentrations a_0 and b_0 in the feed stream at the entrance to the catalyst bed. Hence, $a = a_0$ and $b = b_0$ for $\xi = 1$ as θ varies, and $c = a_0 - b_0$, a constant or a function of θ .

By substituting into Equation (19) one finds:

$$\frac{\partial b}{\partial \xi} = \frac{-k_c}{k_p (\theta + \xi - 1)} \left(\frac{b + a_0 - b_0}{b} \right)^{1/2} \quad (21)$$

The variables in this equation, b and ξ , may be separated and the integration can be carried out to give

$$\begin{aligned} & [(a_0 - b_0)/2] \ln[(\sqrt{a} - \sqrt{b})(\sqrt{a_0} + \sqrt{b_0})/(\sqrt{a_0} - \sqrt{b_0})(\sqrt{a} + \sqrt{b})] \\ & + \sqrt{ab} - \sqrt{a_0 b_0} = -(k_c/k_p) \ln[(\xi + \theta - 1)/\theta] \quad , \quad (22) \end{aligned}$$

with

$$a = b + a_0 - b_0 \quad .$$

If $a_0 = b_0$, that is, equimolar reactant concentration, Equation (22) reduces to

$$b - b_0 = -(k_c/k_p) \ln[(\xi + \theta - 1)/\theta] \quad (23)$$

For the late-time approximation, when $\theta \gg \xi$, the logarithmic term simplifies to:

$$\ln[(\xi + \theta - 1)/\theta] = (\xi - 1)/\theta$$

and Equation (22) is reduced to:

$$a_o - a = b_o - b = (k_c/k_p) \sqrt{a_o/b_o} (\xi - 1)/\theta \quad (24)$$

Equation (24) can be rearranged into a form suitable for graphical analysis and evaluation of the rate constants k_c and k_p by selecting the conditions prevailing at the exit of the catalyst bed ($x = L$):

$$\frac{b_o - b}{\alpha} = \frac{[\exp(k_p s_o/U)] - 1}{\exp(k_p n_o t)} \quad (25)$$

with $\alpha = k_c \sqrt{a_o/b_o}/k_p$, $L/V = 1/U$, the reciprocal space velocity, and $t \gg 1/U$. Thus, at long exposure times, a plot of the logarithm of the amount of reactant converted as a function of time yields a straight line whose slope is equal to $-k_p n_o$.

The intercept I of the resulting straight line (at $t = 0$) is given by

$$I = (b_o - b)_i = \alpha [\exp(k_p s_o/U)] - 1 \quad (26)$$

so that k_p may be evaluated if s_o is known. As observed in previous work, the active site density of the catalyst for methanation and sulfur poisoning is equal to the CO-adsorptive capacity of the catalyst. Thus we may determine s_o from a measurement of the CO-saturation coverage for each of the catalysts under study and evaluate the term α in equation (26). Once k_p has been determined by graphical analysis as prescribed by equation (25), the remaining unknown, the rate constant for methanation k_c , can be calculated.

For interpretation of the experimental results obtained at constant conversion but varying space velocity due to catalyst deactivation, the

following form of equation (25) is found to be useful:

$$\frac{1}{U} = \frac{n_o t}{s_o} + \frac{1}{k_p s_o} \ln \left[\frac{(b_o - b)}{(k_c/k_p)(a_o/b_o)^{1/2}} \right] \quad (27)$$

Equation (27) predicts that the reciprocal space velocity will be a linear function of time. The slope of the plot of $1/U$ versus t represents the ratio of feedstock H_2S concentration to active site density on the fresh catalyst (n_o/s_o), whereas the intercept is a function of the kinetic parameters, including k_p . This analysis may be used to evaluate k_p from the experimental data obtained by adjusting the space velocity to yield constant conversion to methane with progressive catalyst poisoning. At two different levels of reactant conversion kept constant during experiments with a given catalyst, the ratio of the intercepts I_1 and I_2 of equation (27) yields

$$\frac{f'_1 b_{o1}}{f'_2 b_{o2}} = \exp[k_p (I_1 s_{o1} - I_2 s_{o2})] \quad (28)$$

where $f' \equiv (b_o - b)/b_o$ is the fractional conversion of CO to CH_4 and the subscripts (1) and (2) refer to the two conversion levels. This equation is valid when the composition of the feed and the methanation rate constant are identical in the two experiments. These conditions were met in the experimental measurements described in Section III.B.2.

D. Interpretation of Experimental Data

Qualitatively, the difference in catalyst performance between Ni/Al_2O_3 and $Ir/Ni/Al_2O_3$ is quite apparent from the results presented in Section III.B. Both an increase in methanation activity per unit mass of catalyst and an increase in sulfur resistance (as manifested by longer life in the presence of H_2S -containing feed gas) are exhibited by the Ir-promoted catalyst.

With the aid of the theoretical analysis presented in Section III.C, we are able to derive quantitative kinetic data--that is, the rate constants for catalyst deactivation and catalytic methanation. Based

on equation (25), we have replotted in Figure 22 the data from Figure 15. These data show the decline in fractional conversion to methane in a fixed bed reactor with constant inlet conditions during exposure to the syn gas feedstream containing hydrogen sulfide. As deduced from the theoretical model, the experimental data exhibit a logarithmic decay in conversion with exposure. The rate constant for catalyst poisoning k_p , can be evaluated from the slopes of the lines. The results are presented in Table 6.

An alternative evaluation of the poisoning rate constants may be derived from the experiments in which the methane conversion was kept constant by varying the space velocity as catalyst deactivation proceeded (Section III.B.2). As required by the theoretical analysis, we have replotted the data from Figures 16 and 17 in terms of the change in reciprocal space velocity with exposure to feed gas (Figures 23 and 24). This analysis yields the poisoning rate constants shown in Table 7. Also, from this set of measurements we are able to calculate the acceptor site density for sulfur (Table 8). Using these values for s_o , we evaluated the rate constant for methanation, k_c , from the experimental data obtained with constant inlet conditions as well as with variable space velocity (Table 9).

Of interest is the close correlation between the acceptor site density of the catalysts measured for sulfur and carbon monoxide adsorption (Table 8). It may be concluded that both species compete for the same surface sites. Since CO dissociation is known to be a primary step in methanation,⁵ the decay in catalytic activity is undoubtedly due to the loss of these metal sites by irreversible sulfur adsorption and their consequent elimination as CO adsorption sites.

Each set of rate constants for catalyst poisoning and for methanation exhibits some variation, depending on the experimental procedure used. However, it is quite apparent that the Ir-promoted catalyst has significantly higher tolerance to sulfur poisoning and also higher methanation activity. The relative magnitude of the increase in these two parameters is greater than the increase in active surface-site density.

IV PROCESS DESIGN CONSIDERATIONS FOR CATALYTIC METHANATION

A. Effect of Pore Diffusion on a Catalytic Reaction with Negative Reaction Order

Pore diffusion affects the overall (global) rate of a reactant-inhibited reaction, such as the methanation reaction under study. Under conditions for which the reaction rate varies as $P_{CO}^{-1/2}$ (cf. Section II.C), diffusional gradients will lower the CO concentration within the catalyst particle, thereby diminishing the inhibition caused by CO. As a result, the volume average rate could be higher than the rate on the outside surface of the particle. If the diffusivity is very low, the reaction ultimately is confined to a shell near the surface of the particle with virtually no CO (and reaction) in the interior. Using the CO site-competition model of the methanation (ME) rate derived in the text, we can calculate concentration profiles within a hypothetical catalyst pore and estimate the effect of pore diffusion on the observed rate. External diffusion gradients and thermal gradients are taken to be insignificant in the following analysis.

The extent to which pore (intraparticle) diffusion controls the observed global reaction rate is generally described in terms of the effectiveness factor η , which denotes the ratio of the diffusion-limited reaction rate to the expected rate in the absence of pore diffusion gradients.^{24,25} The effectiveness factor depends on the nature of the reaction kinetics, the pore structure, and the Thiele modulus, ϕ , where²⁶

$$\phi = \frac{L}{2} \sqrt{\frac{R \cdot \rho_p}{\rho_g P D_c}} \quad (29)$$

and $1/2 L$ is the characteristic pore length

R is the reaction rate in moles per second per gram of catalyst

ρ_p is the density of the catalyst particle in $\text{g}\cdot\text{cm}^{-3}$

ρ_g is the gas phase density in $\text{mol} \cdot \text{cm}^{-3} \cdot \text{MPa}^{-1}$ at the particle surface

P is the partial pressure of CO in MPa

D_e is the effective pore diffusivity in $\text{cm}^2 \cdot \text{s}^{-1}$.

The observed rate is the volume-average rate, but it is governed in part by the gradient at the surface of the particle. Thus,

$$\eta = \left(\frac{dP}{dz} \right)_{z=0} \left(\frac{\rho_g A D_e}{\rho_p R} \right)_{z=0} \quad (30)$$

where A is the surface area and $(dP/dz)_{z=0}$ is the gradient at the outside edge of the particle.

For slab particles (with outside edges at $z = 0$ and $z = L$), we can solve the diffusion equation

$$\rho_g D_e \frac{d^2 P}{dz^2} = R \rho_p, \quad (31)$$

where $P = P_0$ at $z = 0$ and $dP/dz = 0$ at $z = L/2$. From the solution of P versus z from equation (31), we can determine dP/dz at $z = 0$ and calculate η . As shown in Section II.C, the ME rate is given by:

$$R = W_s k_d (\sqrt{1 + 8K_e P} - 1)^3 / (8K_e P)^2 \quad (32)$$

where W_0 is the catalyst site density. Substituting $z = \xi \frac{L}{2}$, $X = 8K_e P$, and R into equation (31), we have

$$\frac{d^2 X}{d\xi^2} = - \left(\frac{\gamma^2}{2} \right) \frac{(\sqrt{1 + X} - 1)^3}{X^2} \quad (33)$$

with boundary conditions, $X = X_0$ at $\xi = 0$ and $dX/d\xi = 0$ at $\xi = 1$, and where $\gamma = 2\sqrt{W_s k_d \rho_p K_e L^2 / (D_e / \rho_g)}$, Equation (33) can be integrated to give $dX/d\xi$ as a function of X; thus,

$$\frac{dX}{d\xi} = \gamma Y(X) \quad (34)$$

where

$$Y(X) = \{ 2(\sqrt{1+X} - \sqrt{1+X_1}) - 4[1/(\sqrt{1+X} + 1) - 1/(\sqrt{1+X_1} + 1)] - 6 \ln[(\sqrt{1+X} + 1)/(\sqrt{1+X_1} + 1)] \}$$

and $X_1 = 8 K_e P$, at $\xi = 1$, $z = L/2$. Note that $Y(X_0)$ allows us to determine the gradient at the particle surface, since at $X = \xi = 0$, $dP/dz = (1/4 K_e L) dX/d\xi$. Unfortunately we need to know P at $z = L/2$ in order to calculate $Y(X_0)$. However, we can solve equation (34) with ξ as the dependent variable; thus,

$$\xi = \int_{X_0}^X \frac{dx}{\gamma Y(X)}, \quad (35)$$

relating X and ξ and hence providing the P_{CO} versus z profile within the catalyst particle. X_1 is determined from equation (35) for $\xi = 1$; however, we can easily compute the integral in equation (35) by specifying X_1 first. Then we must have

$$\gamma = \int_{X_0}^{X_1} \frac{dx}{Y(X)} = 2 \left[\rho_p W_s k_d K_e L^2 / \rho_g D_e \right]^{1/2} \quad (36)$$

in order that $8K_e P = X_1$ at $z = L/2$. Finally from equations (29), (30) and (32)

$$\phi = (\gamma/\sqrt{2}) [(\sqrt{1+X_0} - 1)/X_0]^{3/2} \quad (37)$$

$$\eta = [2Y(X_0)/\gamma] X_0^2 (\sqrt{1+X_0} - 1)^3 \quad (38)$$

where $Y(X_0)$, γ , ϕ , and η are determined by X_0 and the parameter X_1 .

By varying X_1 over a wide range for several given values of $X_0 = 8K_e P$, we generate the curves relating η and ϕ (Figure 25). For $\phi < 0.5$, η is approximately unity regardless of P_{CO} ; for $\phi > 2$, η gradually approaches the value for a simple first-order reaction²⁴ [$\eta = (\tanh \phi)/\phi$], although the effectiveness factor is always greater for larger values of X_0 . For intermediate values of ϕ and with $X_0 \geq 10$, the effectiveness factor may exceed unity reaching a maximum at approximately $\phi = 1$. The value of η at the maximum increases with increasing X_0 . Isothermal

multiplicity is indicated for $X_0 \geq 200$. The effectiveness factor exceeds unity because the CO concentration in the interior of the particle is lowered, thereby increasing the volume-averaged rate.

To apply these results to our study of the methanation kinetics, we need to estimate ϕ and $K_e P$ in order to evaluate the effectiveness factor. The Thiele modulus ϕ can be estimated from known properties of the catalyst particles and the observed reaction rate (R_{obs}). First we transform the results of Figure 25 to spherical geometry²⁷ by letting $L/2 = r_p/3$; thus,

$$\phi \cong \frac{r_p}{3} \sqrt{\left(\frac{\rho_p}{\rho_g}\right) \frac{R_{obs}}{P D_e}}, \quad (39)$$

The effective diffusion coefficient is related to the Knudsen and molecular diffusion coefficients via

$$D_e = \frac{\epsilon_p}{\tau} \left(\frac{1}{D_m} + \frac{1}{D_k} \right)^{-1} \quad (40)$$

where ϵ_p is the fraction of voids within the catalyst particle

τ is the tortuosity factor

D_m is the molecular diffusion coefficient for the reactant in the gas phase

$D_k = (\bar{v}/3) (2 r_{pore})$ is the knudsen diffusion coefficient in which r_{pore} is the mean pore radius and

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}} \quad \text{is the average molecular velocity.}$$

After substitution into equation (39), we have

$$\phi = 0.035 \left[(R_{obs}/P) (1 + 0.58 P_T)^{-1} \right]^{1/2} \quad (41)$$

where we have taken

$$\begin{aligned} T &= 550 \text{ K} \\ r_{pore} &= 1.0 \times 10^{-6} \text{ cm} \\ D_k &= 4.5 \times 10^{-2} \text{ cm}^2 \cdot \text{s}^{-1} \text{ for CO} \end{aligned}$$

$$D_m = 7.4 \cdot P_T^{-1} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{MPa}^{-1} \text{ for CO in CH}_4^{30}$$

$$\tau = 5.0$$

$$\epsilon_p = 0.4$$

$$\rho_p = 2.62 \text{ g/cm}^3$$

$$D_e = 3.44 \times 10^{-3} (1 + 0.58 P_T)^{-1} \text{ cm}^2/\text{s}$$

$$\frac{L}{2} = \frac{r_p}{3} = 0.0108 \text{ cm}$$

and the total pressure P_T is in MPa, and the rate in $\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$. From equation (41), we see that diffusional transport limitations are more severe at higher total pressure, and $\phi > 1$ for $R_{\text{obs}}/P_{\text{CO}} > 3940 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1} \cdot \text{MPa}^{-1}$ at 0.1 MPa whereas $\phi > 1$ for $R_{\text{obs}}/P_{\text{CO}} > 1930$ at 2.0 MPa.

B. Diffusion-Limited Kinetics in Catalyst Poisoning

To quantitatively compare the tolerance of the promoted and unpromoted catalysts to poisons in the feedstock, it is important to assess the effect of diffusion within the pores of a commercial catalyst pellet on the effective methanation rate. In the following analysis we estimate the effect of the presence of an irreversibly adsorbed poison on catalyst life by evaluating the effect of accumulation of poison on the net reaction rate of the catalyst particle.

Consider diffusion of a gaseous reactant with diffusivity, $D_e (\text{cm}^2 \cdot \text{s}^{-1})$, through a cylindrical pore with radius r and length L . The poison is allowed to adsorb rapidly and irreversibly, completely covering the active surface from the pore mouth to a distance l into the pore. The reaction rate for a partially poisoned particle with this pore geometry is given by the expression,²⁴

$$\text{Rate}_p = \eta_\ell R_\ell \rho_\ell V_\ell \quad (42)$$

where

V_ℓ is the unpoisoned volume,

ρ_p is the particle density, and

η_ℓ and R_ℓ are the effectiveness factor and reaction rate (in $\mu\text{mol/g}\cdot\text{s}$) over the internal region of the catalyst particle from ℓ to L .

From Section IV.A,

$$R_\ell = W_s K_d (\sqrt{1 + 8K_e P_\ell} - 3)^3 / (8K_e P_\ell)^2 \quad (43)$$

$$\phi_\ell = [(L - \ell)/2] (R_\ell \rho_p / \rho_g P_\ell D_e)^{1/2} \quad (44)$$

and

η_ℓ is a function of ϕ_ℓ and $8K_e P_\ell$ (Figure 25).

Now L is approximately $1/3$ the mean catalyst diameter and therefore the rate per catalyst particle is

$$\text{Rate}_p = (4\pi/3) \cdot (3/2)^3 (L - \ell)^3 \eta_\ell R_\ell \rho_p \quad (45)$$

But diffusion through the poisoned zone must equal the rate of a particle,

$$\text{Rate}_p = 4\pi(3/2)^2 (L - \ell)^2 \rho_g D_e (P_o - P_\ell)/\ell \quad (46)$$

and therefore,

$$P_o - P_\ell = [\ell(L - \ell)/2] (\rho_p/\rho_g D_e) \eta_\ell R_\ell \quad (47)$$

Given P_o , T , and ℓ , equation (47) defines P_ℓ and hence the rate from equation (46), and we can evaluate the effect increasing ℓ/L has on the reaction rate of a catalyst particle.

The net reaction for the $\text{Ni}/\text{Al}_2\text{O}_3$ and $\text{Ni} + \text{Ir}/\text{Al}_2\text{O}_3$ catalysts as a function of the extent of poisoning of commercial-sized catalyst

particles have been evaluated (Table 10). Using the following parameters:

$$\begin{array}{ll}
 T = 550 \text{ K} & D_e = 0.034 \text{ cm}^2/\text{s} \\
 P_o = 0.06 \text{ MPa} & \rho_p = 2.62 \text{ g/cm}^3 \\
 P_T = 2.0 \text{ MPa} & \rho_g = 22 \text{ } \mu\text{mol/atm}\cdot\text{cm}^3 \\
 K_\theta = 3280 \text{ MPa}^{-1} & k_{dW_s} = 600 \text{ } \mu\text{mol/g}\cdot\text{s Ni/Al}_2\text{O}_3 \\
 L = 0.2 \text{ cm} & k_{dW_s} = 1200 \text{ } \mu\text{mol/g}\cdot\text{s Ni/Ir/Al}_2\text{O}_3
 \end{array}$$

In general, diffusion limitations (given identical pore geometries) will tend to reduce the differences in activity and poisoning tolerance between a more active and a less active catalyst. It is evident from the theoretical analysis (Table 10) that the initial activity of the promoted catalyst is about 50% greater than that of the unpromoted catalyst under conditions of diffusion-limited kinetics, despite a 3 to 1 ratio of methanation activity in the absence of such limitations. For maximum use of the superior properties of the Ir-promoted catalyst, its physical properties, such as pellet size and pore volume, should be so modified as to reduce diffusional constraints on the overall reaction rate.

C. Equilibrium Compositions for Combined Methanation and Shift Conversion

In the thermodynamic calculations of the equilibrium gas phase composition, we have included the following gaseous species: CH_4 , H_2O , CO , CO_2 , and H_2 . In accordance with the phase rule, a single-phase, five-component system requires six variables to be specified. We chose the following:

- (1) Total gas pressure ($P = P_{\text{CH}_4} + P_{\text{H}_2\text{O}} + P_{\text{CO}} + P_{\text{CO}_2} + P_{\text{H}_2}$)
- (2) Temperature
- (3) O/H ratio
- (4) C/H ratio
- (5) The methanation equilibrium: $3\text{H}_2 + \text{CO} \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$
- (6) The water gas shift equilibrium: $\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{CO}_2 + \text{H}_2$.

The thermodynamic data for the two reactions were taken from the JANAF thermochemical tables.²⁸ The six simultaneous equations were solved numerically using a program described previously.²⁹ The ideal gas law was taken to apply over the entire pressure range.

The results of the analysis are presented in Table 11 for $1 \leq P \leq 2.5$ MPa and $1 \leq H_2/CO \leq 3$ at 600 K. It is to be noted that the equilibrium conversion to methane is very high. The water gas shift reaction is markedly enhanced with decreasing H_2/CO . At $H_2/CO = 1$, methane and carbon dioxide are the predominant products, as may be described by the stoichiometric equation: $2H_2 + 2CO \rightleftharpoons CH_4 + CO_2$. The data suggest that at this temperature the reverse water gas shift reaction makes only a small contribution.

V CONCLUSIONS

The results of this study demonstrate that the Ir/Ni/Al₂O₃ catalyst possesses several valuable and superior characteristics when used for catalytic methanation under typical industrial conditions.

These properties include:

- Higher activity by a factor of > 2 than that of the unpromoted Ni/Al₂O₃ catalyst.
- Enhanced resistance to deactivation by hydrogen sulfide during exposure to contaminated feedstock, as manifested by the prolonged high methanation activity in the extended service lifetime up to twice that of the unpromoted catalyst.
- High resistance to carbon fouling.

VI RECOMMENDATIONS

Further assessment and development of the promoted catalyst for use in the catalytic methanation of carbon monoxide should include the following experimental investigations:

1. Evaluation of the methanation activity and sulfur-resistance of catalyst formulations containing substantially less than 1 wt% of iridium. Preliminary tests have suggested that the superior properties of the promoted catalyst can be secured with the addition of as little as 0.1% iridium.
2. An extension of the performance tests of the promoted catalyst for shift-methanation service. Carbon fouling of nickel catalysts, occurs with feedstocks having $H_2/CO < 2.6$. The promoted catalyst appears to possess higher resistance to carbon fouling, and may be well suited to use with such feedstocks.
3. Also, the concurrent hydrogenation of CO in admixture with CO_2 warrants experimental study.

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Table 1

LEAST-SQUARES REGRESSION ANALYSIS FOR METHANATION
CATALYZED BY Ni/Al₂O₃ AND Ni-Ir/Al₂O₃^a

	<u>Sulfur-Free</u>		<u>Sulfur-Poisoned</u>	
	<u>Ni/Al₂O₃</u>	<u>Ni-Ir/Al₂O₃</u>	<u>Ni/Al₂O₃</u>	<u>Ni-Ir/Al₂O₃</u>
No. of data points	7	11	19	17
E, activation energy (kJ/mol)	159.0	130.0	127.4	111.2
y, power law coefficient for CO	- 0.48	- 0.41	- 0.45	- 0.39
A, intercept (μmol/g·s)	5.98 x 10 ¹⁵	1.35 x 10 ¹³	7.03 x 10 ¹¹	1.36 x 10 ¹¹
Standard deviation for E (kJ/mol)	± 12.2	± 12.6	± 12.8	± 7.7
Correlation coefficient for E	0.997	0.995	0.995	0.998
Standard deviation for y	± 0.05	± 0.12	± 0.14	± 0.09
Correlation coefficient for y	0.995	0.962	0.955	0.974
Net standard deviation for ln rate ^b	± 0.039	± 0.068	± 0.096	± 0.074
Calculated rate (μmol/g·s) ^c	14.3	21.4	1.6	9.2

^aRate expression: $\ln \left(R_{\text{CH}_4} \right) = \ln A - E \left(\frac{1}{T} \right) + y \ln P_{\text{CO}}$

^b $\sigma = \sqrt{\Sigma (R_i - R_{\text{calc}})^2 / (n - 3)}$

^cAt 550 K and $P_{\text{CO}} = 1 \times 10^4$ Pa

Table 2

LEAST-SQUARES ANALYSIS OF C₂H₆ FORMATION RATES FOR
Ni/Al₂O₃ AND Ni-Ir/Al₂O₃ CATALYSTS

Catalyst	Temperature (K)	Total Pressure (atm)	H ₂ Pressure (atm)	No. of Data Points	Exponent ^a (y)	Correlation Coefficient	First-Order Rate Constant (μmol/g·s·atm)
Ni-Ir-Al ₂ O ₃	525.8 ± 0.1	5.4	4.8 ± 0.1	4	1.26 ± 0.24	0.982	2.08 ± 0.48
	556.0 ± 0.1	5.1	4.1 ± 0.1	5	1.15 ± 0.18	0.987	2.37 ± 0.25
	550.6 ± 2.2	21.5	16.5 ± 1.5	16	1.26 ± 0.28	0.977	1.85 ± 0.58
Ni/Al ₂ O ₃	533.1 ± 0.8	5.3	4.7 ± 0.1	16	0.96 ± 0.31	0.951	2.05 ± 0.29
	575.5 ± 1.0	21.5	18.0 ± 0.5	17	1.16 ± 0.18	0.989	1.21 ± 0.29
	580.0 ± 0.8	5.1	4.2 ± 0.2	5	1.20 ± 0.30	0.961	2.70 ± 0.60

^a According to the power law, Rate C₂H₆ = k · P_{CO}^y

^b The first-order rate constant was taken at k = Rate_{C₂H₆} / P_{CO}.

Table 3

SUMMARY OF CATALYST TEST PARAMETERS WITH FIXED BED REACTORS

Experiments →	Methanation			Shift-Methanation
	Fixed Inlet Conditions	Constant Conversion	Long Term Tests	
Reactor:				
Material	Pyrex	Stainless Steel	Stainless Steel	Pyrex
Geometry	Microreactor	1.09 cm ID Tube with Axial Thermowell	1.9 cm ID Tube (see Fig. 14)	Microreactor
Pressure (Pa x 10 ⁻⁵ /psig)	1.65/8.8	4.48/50	4.48/50	1.03/0
Inlet Temperature (K)	540	530	533	570-723
Catalyst:				
Mass (g)	0.03	0.06	5.6	0.05-0.07
Particle Size (mm)	0.06-0.09	0.5-0.8	0.5-0.8	0.06-0.09
Bed Depth (mm)	thin	30	96	thin
Diluent	none	α -Al ₂ O ₃	α -Al ₂ O ₃	none
Diluent/Catalyst (V/V)	-	50	4	-
Feedstock:				
Syn Gas H ₂ /CO (mole/mole)	3	3	3	1.6-2.1
Inert	N ₂	N ₂	N ₂	none
Inert/Syn Gas (mole/mole)	7.7	11	7.1	-
Contaminants (separate runs)	H ₂ S	H ₂ S/NH ₃	H ₂ S	none
Contaminant Level (ppm)	0.5	0.4/900	0.6-1.5	0
Space Velocity (NTP) (hr ⁻¹ x 10 ⁻⁴)	70	11-68	0.67	17-20

Table 4

SURFACE ANALYSIS OF CATALYST SAMPLES BY
AUGER ELECTRON SPECTROSCOPY (AES)

Reactor	Solid Phase	Location in Bed	Level of Component ^a		
			Sulfur	Nickel	S/Ni
A	1Ir/25Ni/ Al ₂ O ₃ ^b	top	2.4 ± 0.14	1.6 ± 0.21	1.5
		bottom	1.6 ± 0.21	1.9 ± 0.28	0.84
B	25Ni/Al ₂ O ₃ ^b	top	1.8 ± 0.85	0.85 ± 0.50	2.1
		bottom	1.5 ± 0.87	1.1 ± 0.34	1.4

^aAES peak heights were corrected for Auger electron yield on the basis of empirical calibrations with pure substances as standards, then normalized to Al (1396 eV) peak height. For all samples O/Al (peak height ratio) = 1.5 ± 0.1, which corresponds to Al₂O₃.

^bNumbers refer to metal loading in wt percent.

Table 5

THE ROLE OF THE WATER GAS SHIFT REACTION IN
CATALYTIC METHANATION (P = 1 atm)

Catalyst	Temperature (K)	GHSV (hr ⁻¹ x 10 ⁻⁵)	Duration of Run (hr)	Feedstock (mol·cm ⁻³)x10 ⁶				Product (mol·cm ⁻³)x10 ⁶			
				CO	H ₂	He	H ₂ O	CO	CH ₄	CO ₂	CO ₂ /CH ₄
25Ni/Al ₂ O ₃	723	2.0	1	3.45	7.25	30.2	0	1.01	1.27	1.06	0.83
	723	2.0	1	3.45	7.25	30.2	0.87	0.87	1.34	1.28	0.96
1Ir/25Ni/Al ₂ O ₃	723	2.0	1	3.45	7.25	30.2	0	0.74	1.47	1.17	0.80
	723	2.0	1	3.45	7.25	30.2	0.87	0.74	1.39	1.20	0.89
	573	1.7	15	7.58	12.1	14.1	0.49	7.42	0.095	0.0036	0.04

Table 6

RATE CONSTANT FOR CATALYST POISONING BY
H₂S FROM EXPERIMENTS WITH CONSTANT INLET CONDITIONS *

Catalyst	k_p	
	$(s^{-1} \cdot ppm_{H_2S}^{-1})$	$[s^{-1} \cdot (mol/cc)_{H_2S}^{-1}] \times 10^{-5}$
25 Ni/Al ₂ O ₃	5.3	7.5
1Ir/25Ni/Al ₂ O ₃	2.0	2.8

* See Table 3.

Table 7

RATE CONSTANT FOR CATALYST POISONING FROM
CONSTANT CONVERSION EXPERIMENTS *

Catalyst	k_p	
	$(s^{-1} \cdot ppm_{H_2S}^{-1}) \times 10^5$	$[s^{-1} \cdot (mol/cc)_{H_2S}^{-1}] \times 10^{-5}$
25 Ni/Al ₂ O ₃	10.3	5.8
1Ir/25Ni/Al ₂ O ₃	6.5	3.0

* See Table 3.

Table 8

ACCEPTOR SITE DENSITY FOR
SULFUR POISON

Catalyst *	Acceptor Site Density (mol/g cat) x 10 ⁶	
	Sulfur Adsorbed [†]	CO Adsorbed
25Ni/Al ₂ O ₃	90	96
1Ir/25Ni/Al ₂ O ₃	120	146

* Numbers depict metal loading (wt%)

[†] Evaluated from loss in methanation activity due to H₂S exposure.

Table 9

RATE CONSTANT FOR METHANATION

Catalyst	Rate Constant k _c (s ⁻¹)	
	Constant Conditions*	Variable Space Velocity*
25Ni/Al ₂ O ₃	0.23	0.22
1Ir/25Ni/Al ₂ O ₃	0.38	0.53

* See Table 3.

Table 10

THE EFFECT OF SULFUR POISONING ON THE METHANE
FORMATION RATE FOR $\text{Ni}/\text{Al}_2\text{O}_3$ AND $\text{Ir} + \text{Ni}/\text{Al}_2\text{O}_3$ PELLETS

$\text{Ir}/\text{Ni}/\text{Al}_2\text{O}_3$		$\text{Ni}/\text{Al}_2\text{O}_3$	
Rate ($\mu\text{mol}/\text{g}\cdot\text{s}$)	Time (hr)	Rate ($\mu\text{mol}/\text{g}\cdot\text{s}$)	Time (hr)
20.6	0	13.1	0
18.5	0.35	11.9	0.23
15.6	1.39	11.0	0.93
10.5	8.7	8.32	5.80
7.60	20.0	5.11	23.2
5.87	34.8	3.56	50.0
2.49	139	2.36	92.8
0.40	870	0.39	580
0.04	2230	0.04	1480
0.00	3480	0.00	2320

$T = 550 \text{ K}$; $P_{\text{CO}} = 0.06 \text{ MPa}$; $P_{\text{T}} = 2.0 \text{ MPa}$

$P_{\text{H}_2\text{S}} = 0.2 \text{ Pa}$; Pellet diameter = 0.6 cm

Table 11

EQUILIBRIUM COMPOSITION FOR COMBINED METHANATION AND SHIFT CONVERSION

H_2/CO	P (MPa)	T (K)	Equilibrium Mole Fraction					Mole Fraction Ratio	
			H_2	CO	H_2O	CO_2	CH_4	$\frac{CH_4}{H_2O}$	$\frac{CH_4}{CO_2}$
3	0.1	600	0.0453	0.0000	0.466	0.0113	0.477	1.02	42.2
	1.5		0.0157	0.0000	0.488	0.0039	0.492	1.01	126.1
	2.5		0.0128	0.0000	0.490	0.0032	0.494	1.01	154.4
2	0.1	600	0.0192	0.00035	0.321	0.170	0.490	1.53	2.88
	1.5		0.0051	0.00009	0.330	0.167	0.497	1.51	2.98
	2.5		0.0059	0.00007	0.331	0.167	0.498	1.50	2.98
1	0.1	600	0.00147	0.00788	0.00321	0.492	0.495	154.7	1.00
	1.5		0.000251	0.0031	0.00142	0.497	0.498	355.7	1.00
	2.5		0.000181	0.0026	0.00121	0.497	0.499	415.8	1.00
3	0.1	700	0.146	0.0014	0.391	0.0355	0.426	1.09	12.00
	1.5		0.0538	0.00016	0.460	0.0133	0.473	1.03	35.0
	2.5		0.0442	0.00011	0.467	0.0109	0.478	1.04	43
2	0.1	700	0.0843	0.0056	0.279	0.176	0.455	1.64	2.58
	1.5		0.0239	0.0013	0.318	0.170	0.487	1.53	2.87
	2.5		0.0136	0.0010	0.321	0.169	0.490	1.53	2.90
1	0.1	700	0.0150	0.0477	0.0159	0.452	0.468	29.4	1.04
	1.5		0.0029	0.0186	0.0078	0.481	0.489	62.7	1.02
	2.5		0.0021	0.0156	0.0068	0.484	0.491	72.2	1.01

SA-7930-1

FIGURE 1 EXPERIMENTAL SYSTEM FOR KINETIC STUDIES INCLUDING RECYCLE AND FIXED BED REACTORS

SA-7930-2R

FIGURE 2 BERTY REACTOR (A) AND COMPRESSOR (B)

SA-7930-3

FIGURE 3 BERTY AUTOCLAVE

SA-7938-19

FIGURE 4 DEPENDENCE OF METHANATION RATE ON CO PARTIAL PRESSURE
Catalyst: $\text{Ni}/\text{Al}_2\text{O}_3$. Total pressure = 1 atm.

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FIGURE 5 DEPENDENCE OF METHANATION RATE ON CO PARTIAL PRESSURE
Catalyst: Ni-Ir/ Al_2O_3 . Total pressure = 1 atm.

SA-7938-21

FIGURE 6 DEPENDENCE OF METHANATION RATE ON CO PARTIAL PRESSURE
Catalyst: H_2S -EXPOSED $\text{Ni}/\text{Al}_2\text{O}_3$. Total pressure = 1 atm.

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FIGURE 7 DEPENDENCE OF METHANATION RATE ON CO PARTIAL PRESSURE
Catalyst: H₂S-EXPOSED Ni-Ir/Al₂O₃. Total pressure = 1 atm.

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FIGURE 8 RATE OF METHANE FORMATION CATALYZED BY $\text{Ni}/\text{Al}_2\text{O}_3$ OVER A RANGE OF TOTAL PRESSURE

SA-7938-27

FIGURE 9 RATE OF METHANE FORMATION CATALYZED BY Ni-Ir/ Al_2O_3 OVER A RANGE OF TOTAL PRESSURE

SA-7938-23

FIGURE 10 DEPENDENCE OF C_2H_6 FORMATION RATE ON CO PARTIAL PRESSURE

Catalyst: Ni/Al_2O_3

- (a) $\square$ $T = 533 \text{ K}$, $P_{H_2} = 4.7 \pm 1 \text{ atm}$
- (b) $\circ$ $T = 576 \text{ K}$, $P_{H_2} = 18.0 \pm 5 \text{ atm}$
- (c) $\triangle$ $T = 581 \text{ K}$, $P_{H_2} = 4.2 \pm 2 \text{ atm}$

SA-7938-24

FIGURE 11 DEPENDENCE OF C₂H₆ FORMATION RATE ON CO PARTIAL PRESSURE

Catalyst: Ni-Ir/Al₂O₃.

(a) □ T = 526 K, P_{H_2} = 4.8 atm

(b) ◇ T = 551 K, P_{H_2} = 16.5 atm

(c) ○ T = 555 K, P_{H_2} = 4.1 atm

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FIGURE 12 PREDICTED METHANATION RATES WITH AND WITHOUT PORE DIFFUSION VERSUS PARTIAL PRESSURE CO FOR Ni-Ir/Al₂O₃

JA-350543-7

FIGURE 13 FIXED BED REACTOR SYSTEM

SA-7930-4

FIGURE 14 INTEGRAL REACTOR

SA-7930-32

FIGURE 15 CATALYST DEACTIVATION DURING METHANATION

$[\text{H}_2/\text{CO}/\text{N}_2 = 3/1/28; 0.3 \text{ ppm H}_2\text{S}; P = 8.8 \text{ psig } (1.6 \times 10^5 \text{ Pa});$
 Space Velocity = $700,000 \text{ hr}^{-1}$ (194 s^{-1})

JA-350543-8

FIGURE 16. CHANGE IN SPACE VELOCITY WITH CONSTANT CONVERSION TO METHANE

Catalyst: Ni/Al₂O₃. T = 530 K (Values of conversion adjacent to curves.)

[Feed Composition (Vol %): H₂ = 6.3; CO = 2.1, N₂ = 91.6; H₂S = 0.5 ppm]

JA-350543-9

FIGURE 17 CHANGE IN SPACE VELOCITY WITH CONSTANT CONVERSION TO METHANE

Catalyst: Ir/Ni/Al₂O₃. T = 530 K (Values of conversion adjacent to curves.)

[Feed Composition (Vol %): H₂ = 6.3; CO = 2.1, N₂ = 91.6; H₂S = 0.5 ppm]

SA-7930-31

FIGURE 18 OBSERVED TEMPERATURE PROFILE IN CATALYST BEDS
 (Values of maximum ΔT were interpolated from continuous record of temperatures as a function of time.)

SA-7930-30

FIGURE 19 CHANGE IN CATALYTIC ACTIVITY WITH EXPOSURE TO H₂S-CONTAINING FEED GAS

[H₂/CO/N₂ = 3.1/1/7.1; H₂S = 1.3 ppm; Pressure = 50 psig (4.5 x 10⁵ Pa);
Space Velocity = 6700 hr⁻¹]

JA-350543-10

FIGURE 20 EFFECT OF AMMONIA ON CATALYST ACTIVITY
 ($H_2/CO = 3/1$; 1 Vol % NH_3 ; 530 K; Space Velocity: $3 \times 10^5 \text{ hr}^{-1}$)

FIGURE 21 TPSR OF SURFACE CARBON WITH HYDROGEN FOR Ir-PROMOTED AND Ni/Al₂O₃ CATALYSTS (HEATING RATE = 1 K·s⁻¹)

SA-7930-33

FIGURE 22 DECLINE IN METHANATION ACTIVITY AT LONG EXPOSURE TO SYNGAS
 ($H_2/CO/N_2 = 3/1/28$; 0.5 ppm H_2S ; $P = 1.65 \times 10^5$ Pa; Space Velocity = $700,000 \text{ hr}^{-1}$)

9A-7930-35

FIGURE 23 CHANGE IN SPACE VELOCITY WITH TIME AT CONSTANT FRACTIONAL CONVERSION, Ni/Al₂O₃ CATALYST

SA-7930-36

FIGURE 24 CHANGE IN SPACE VELOCITY WITH TIME AT CONSTANT FRACTIONAL CONVERSION, Ir/Ni/Al₂O₃ CATALYST

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FIGURE 25 EFFECTIVENESS FACTOR FOR A REACTANT INHIBITED REACTION