

THE KINETICS OF METHANATION ON NICKEL CATALYSTS

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Abstract An empirical rate equation was obtained for the methanation kinetics catalyzed by MCR–2X, a commercial catalyst prepared by Haldor-Topsoe. The studies were carried out in a fixed-bed reactor under differential conditions, and in a gradientless recycle reactor (Berry) over a range of total pressures, reactant concentrations (H_2/CO ratios), and temperatures. The kinetics of methanation were found to be of first order in hydrogen at total gas pressures below 7 atm, and of half order at higher pressures. With respect to carbon monoxide the reaction order was -0.46 in the composition range studied ($H_2/CO \geq 3$). Water vapor, a reaction product, was observed to inhibit the methanation rate. On the other hand, carbon dioxide and methane had no influence on the reaction kinetics. The following rate equation was obtained for the methanation rate (r_{CH_4}) with the partial pressure (p) of each component expressed in atmospheres and the rate constant k in $\text{mol.g}^{-1}\text{catalyst.s}^{-1}$:

$$r_{CH_4} = 1.5 \times 10^6 \exp(-26000/RT) P_{H_2}^x / (P_{CO}^y + cP_{H_2O}^z)$$

with

$$x = 1 \text{ at } P_{H_2} < 5 \text{ atm}$$

$$x = 0.5 \text{ at } P_{H_2} > 7 \text{ atm}$$

$$y = 0.5$$

$$z = 0.6$$

$$c = 0.42 \text{ atm}^{-0.1}$$

The catalyst was observed to be susceptible to deactivation by hydrogen sulfide in the feed gas. The rate coefficient for deactivation was determined. Its value for MCR–2X was comparable to that of other nickel-based catalysts.

چکیده در این بررسی معادله سینتیک تولید متان با استفاده از کاتالیزور MCR–2X (یک کاتالیزور تجاری) ارائه شده است. مطالعاتی در یک راکتور بستر ثابت (دیفرانسیلی) و یک راکتور برتی (Berry) (دوره‌ای یکنواخت) در شرایط مختلفی از فشار کل، غلظت و دما انجام گردیده است. نتایج حاصله نشان داده که تولید متان در حالتی که فشار کل گاز کمتر از γ اتمسفر باشد نسبت به فشار جزئی نیتروژن از درجه اول بوده و در فشارهای بالاتر این درجه به نصف تقلیل می‌یابد. درجه واکنش نسبت به مونوکسید کربن، با توجه به میزان تغییرات آن در مطالعات حاضر، برابر 0.46 – بدست آمده است. نتیجه نشان داده که یکی از محصولات واکنش یعنی بخار آب سبب کاهش سرعت تولید متان میشود. در حالیکه دی اکسید کربن و متان اثری بر سینتیک واکنش ندارند. همچنین مشاهده شده است که کاتالیزور مزبور نسبت به هیدروژن سولفاید موجود در گاز ورودی حساس بوده و در فعالیت آن کاسته میشود. ضریب کاهش فعالیت در این مورد مشخص شده که مقدار آن قابل مقایسه با ضریب کاتالیزورهای پایه نیکل می‌باشد.

INTRODUCTION

The high exothermic heat of reaction for catalytic methanation provides a useful method for local heat generation, such as in secondary recovery in deep oil wells. For successful development of such a process, the catalyst needs to have high selectivity for methane and high activity to give economic space-

time yields. In addition, the catalysts must be able to tolerate high temperatures without undergoing morphological changes, on the basis of careful examination of a number of catalysts in the previous studies,^[1] the catalyst MCR–2X (manufactured by Haldor-Topsoe) was selected as the material most suitable for the process.

In evaluating the catalytic properties of MCR-2X we used a fixed-bed reactor and a gradientless reactor to determine the methanation kinetics, coking tendency, and sulfur-poisoning kinetics. The experimental measurements were designed to provide fundamental information on reaction kinetics and catalyst performance over a range of operating conditions.

EXPERIMENTAL METHODS

1. Catalyst

The commercial catalyst MCR-2X (supplied by Haldor-Topsoe) was crushed and screened to a particle size range from 0.50 to 0.85 mm

(20 to 32 Tyler mesh size).

2. Fixed-Bed Reactor Studies

For the study of methanation kinetics and catalyst deactivation, a differential reactor was employed. The tests were performed in fixed-bed reactors connected through appropriate valves and tubing to a source of feed gas. The apparatus is shown schematically in Figure (1) The reactors were fabricated from 316 type stainless-steel tubing. They were connected to the test system with standard stainless-steel tubing and fittings.

Feed gas was supplied from cylinders containing premixed gases prepared to our specifications. Pressure was maintained at a constant level independent of flow by conven-

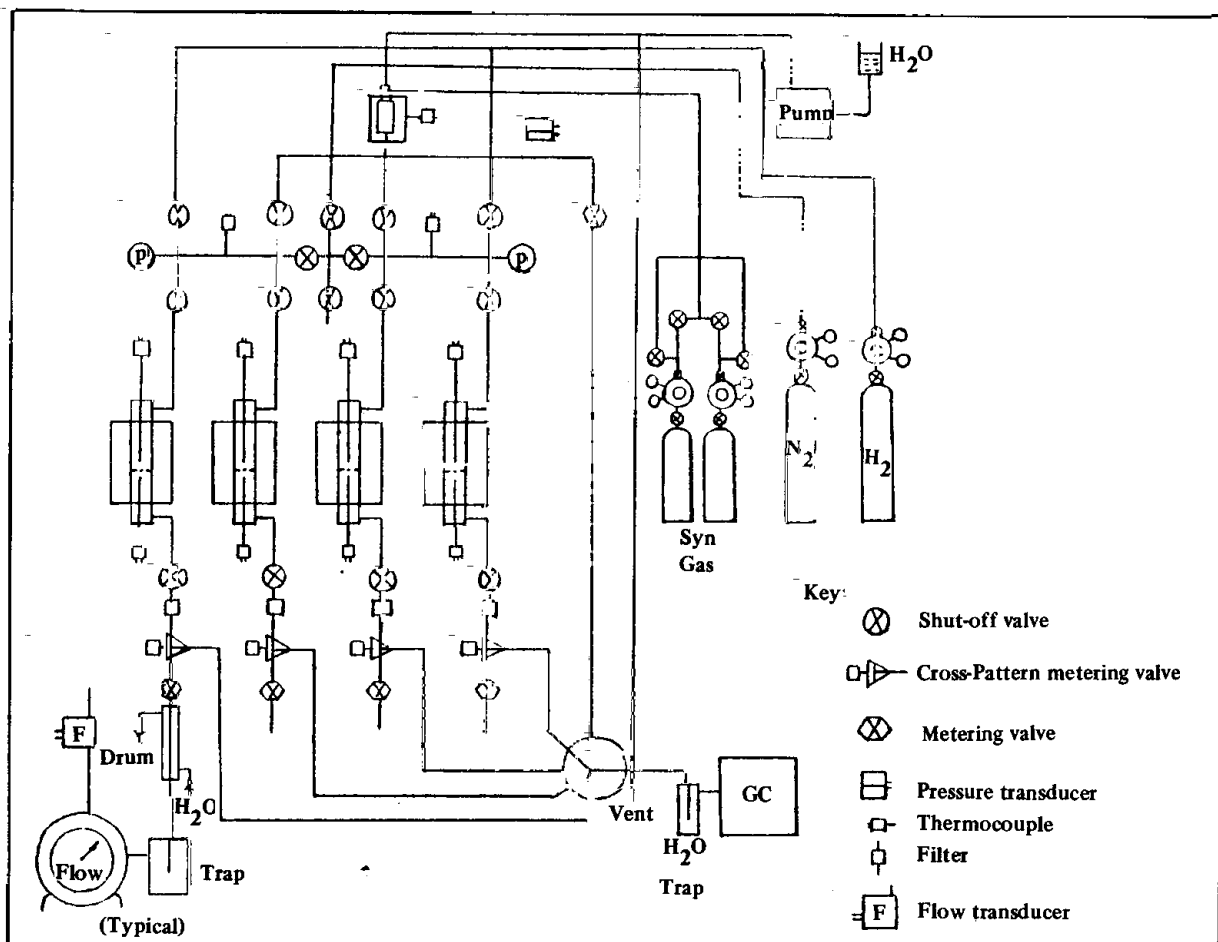


Figure 1. Fixed Bed Reactor System

tional diaphragm regulators on the feed gas cylinders. Flow rate was controlled by adjustment of metering valves at the outlets of the reactors. Gas-flow rates on a "dry basis" were determined at the reactor outlet after condensing and trapping water vapor. Temperatures in the reactor (upstream and downstream of the catalyst bed) were measured with chromel-alumel thermocouples.

The reactor loaded with catalyst was flushed and pressure tested with helium. In situ reduction of the Ni-catalyst consisted of heating the sample in flowing hydrogen (10 cc/min) to 373 K for 2 hours, followed by 723 K for 10 hours (or more). After reduction, the sample was cooled in flowing hydrogen to the desired reaction temperature.

Following this pretreatment, the reactant gas mixture was admitted to the reactor.

After exposure for thirty minutes under reaction condition, the effluent gas was analyzed by gas chromatography. Then the feed gas was replaced by pure hydrogen for one hour. By alternating the reaction periods and reduction periods, called the "hydrogen bracketing technique", stable catalyst activity could be achieved after several cycles. The "hydrogen bracketing technique" provided a most suitable procedure for maintaining a clean metal surface and giving reproducible results.

In the kinetic studies the space velocities used varied from 1 to $10 \times 10^6 \text{ hr}^{-1}$ in order to keep CO conversions at low levels (less than 10 vol%). By operating under differential-reactor conditions, heat and mass transfer effects were minimized, and any significant effects due to product inhibition were eli-

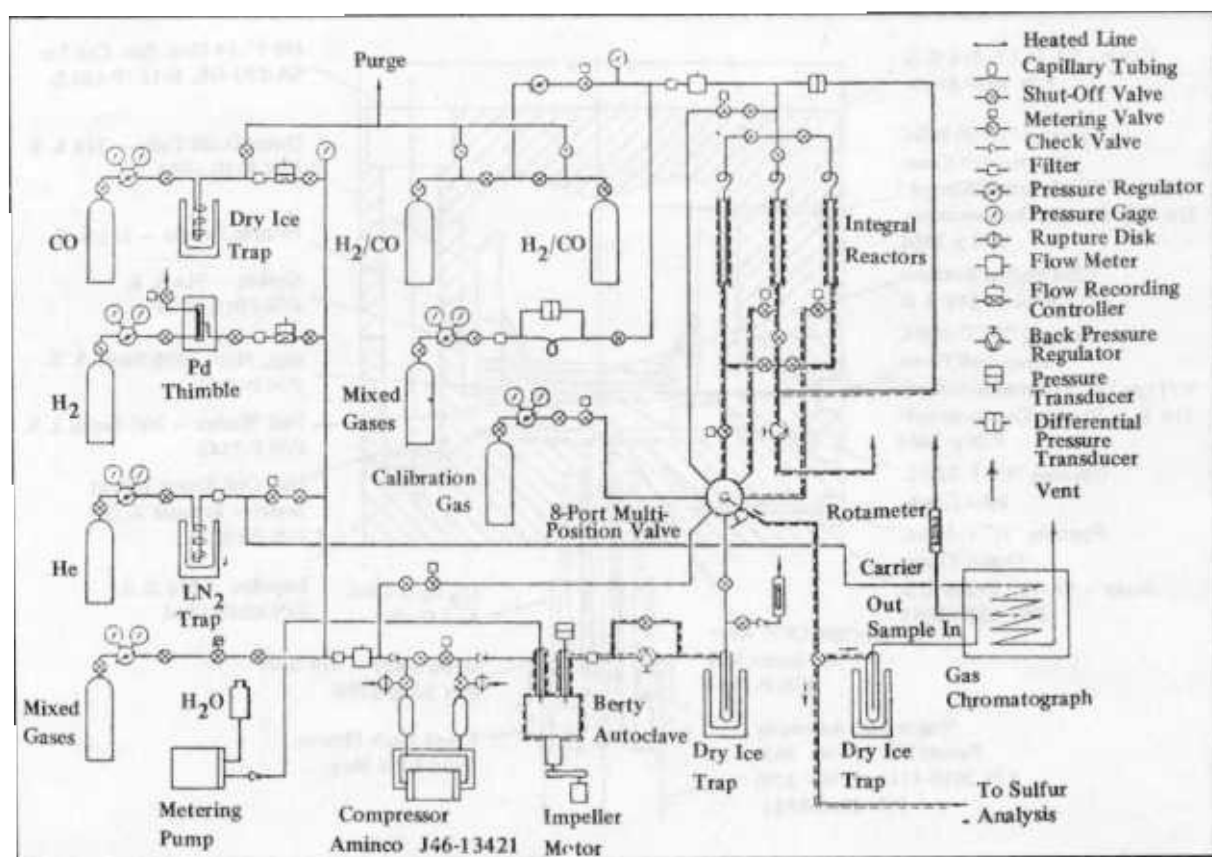


Figure 2. Experimental System for Kinetic Studies Including Recycle and Fixed Bed Reactors.

minated, as discussed in a subsequent section of this report.

Reactant and product gases were analyzed for H₂, CO, CH₄, and CO₂ with a gas chromatograph (GC). The peaks were integrated by means of an electronic digital integrator. The concentration of H₂O in the reactor effluent was calculated from a hydrogen and oxygen balance. The sensitivity of the GC was calibrated empirically by injection of known volumes of each of the chemical components under study.

3. Gradientless Reactor Study

Additional kinetic studies were performed in a high pressure, internal-recycle reactor. The detailed schematic diagram of the apparatus is shown in Figure 2. The feed gases were metered and mixed, and then compressed to the desired pressure at a constant

flow before entering the reactor. The reactor pressure could be adjusted up to 68 atm with a black-pressure regulator (Tescom), which maintained the set pressure to within narrow limits. The gas compositions were adjusted by means of calibrated flow controllers (Tylan). The mass flow rate of each gas stream could be measured to within ± 2 vol%. Steam was introduced into the feed stream by displacing liquid water from a high pressure metering pump and vaporizing it on an electrical heater. The compressor (Aminco) allowed the compression of 25 cm³/sec of feed gas to 45 atm at a suction pressure of 10 atm. Surge tanks (250 cm³) and a by-pass metering valve were used to dampen flow fluctuations and stabilize the suction pressure. The internal recycle Berty Reactor (Figure 4) was manufactured by Autoclave Engineers. By operation at high

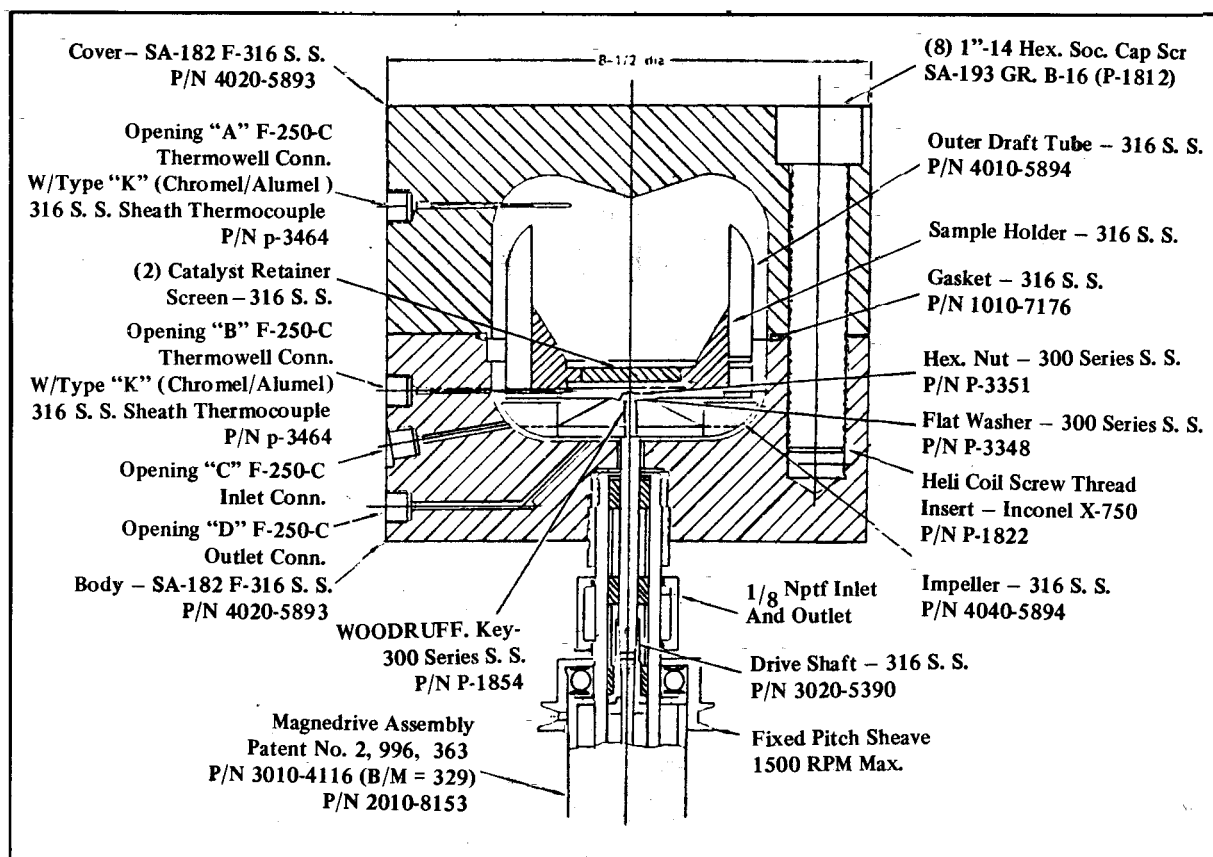


Figure 3. Berty Autoclave

internal recycle ratio (≥ 50), the conversion rate per pass was kept below a specified limit (< 10 V%) and the temperature rise through the bed restricted to less than 3 K. Thermocouples were located 2 cm above and 0.5 cm below the catalyst bed. Their output was monitored continuously. Heat was provided by 3-kw electric elements that were contained in a shroud that surrounded the sides and top of the reactor. Two proportional controllers were capable of controlling the reactor temperature to ± 1 K, by sensing the temperature at two points on the wall of the vessel. However, following a perturbation, such as a change in feed composition or in temperature, the time required to reach steady-state conditions in the reactor was in excess of five hours. All measurements were carried out with an impeller speed of 1800 rpm, which in separate tests had been found to minimize interparticle flow residence during reaction.

In a typical methanation experiment a sample of catalyst was placed in the reactor between two 40-mesh stainless-steel screens. After sealing the reactor it was pressurized to 20 atm in He and checked for leaks. The temperature of the reactor was then raised 723 K in flowing hydrogen to reduce the catalyst.

Subsequently, the reactor was cooled to the desired reaction temperature in flowing hydrogen. All experimental variables were measured after steady-state conditions prevailed. The detailed experimental procedure is described elsewhere. (5).

EXPERIMENTAL RESULTS

1. Effect of CO

The first set of experiments was designed to obtain the dependence of the methanation rate on the partial pressure of carbon monoxide. The results obtained in the gradientless recirculation reactor (Table 1) were analyzed in terms of the empirical rate law

$$r_{\text{CH}_4} = kP_{\text{CO}}^y \quad (1)$$

where k represents the rate coefficient and y the reaction order for $\text{CO}(P_{\text{CO}})$. These measurements were carried out at nearly constant partial pressures of hydrogen and sufficiently high CO pressures, to render the kinetics unaffected by transport limitations. As observed for other Ni-based catalysts, (3) the kinetics exhibited a negative reaction order with respect to CO in the pressure range of interest to our study (Figure 5). By graphical

Table 1 Methanation Rate Dependence on Partial Pressure of Carbon Monoxide Measured in Bertly Reactor at 543 K°

Partial Pressure (atm)					CO Conversion Rate (mol. g ⁻¹ . s ⁻¹) x 10 ⁶	
CO	H ₂	CH ₄	CO ₂	H ₂ O	CO	CH ₄
2.11	24.49	3.67	0.08	3.67	86	84
2.65	25.03	3.03	0.27	2.72	80	75
3.40	23.06	3.65	0.28	3.29	69	64
3.54	22.92	3.63	0.27	3.47	68	63
3.88	23.12	3.03	0.82	2.79	63	61

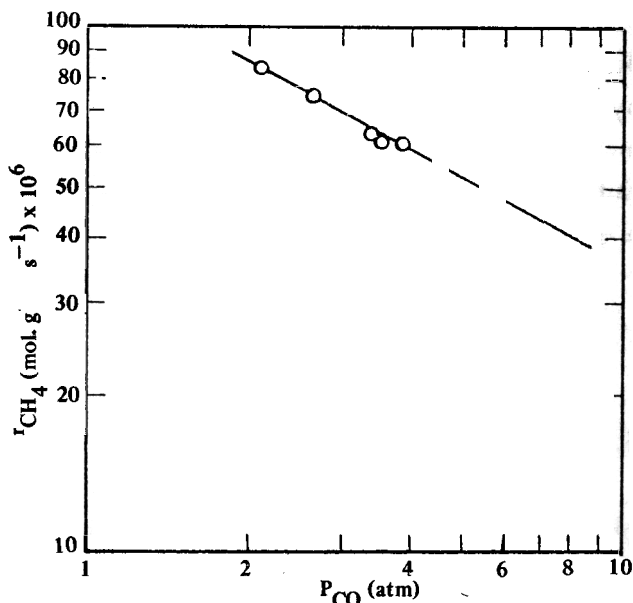


Figure 4. Variation in CO Consumption Rate with CO Pressure.

($T=543$ K; Total Pressure=34 atm; $P_{H_2}=23.7$ atm)

analysis the value of y was found to be -0.46 ± 0.05 . This value compares to $y = -0.43 \pm 0.04$ measured^[2] with another Ni/Al₂O₃ catalyst (Girdler G-65).

2. Effect of H₂

In evaluating the reaction order for hydrogen, the differential reactor was employed in a series of measurements in which the H₂/

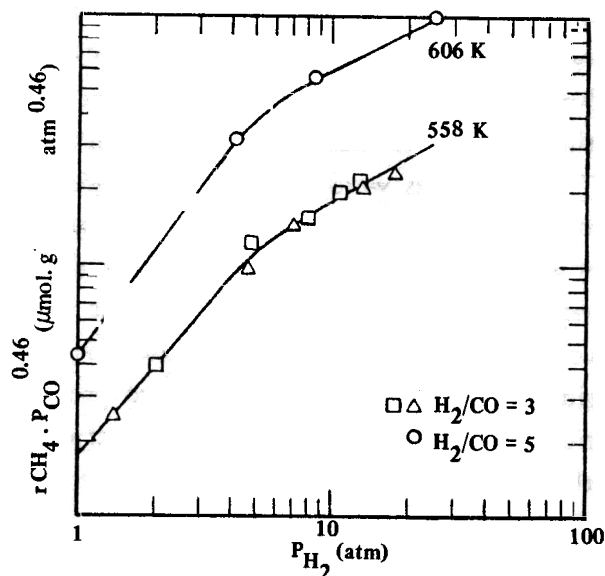


Figure 5. Effect of Partial Pressure of Hydrogen and H₂/CO Ratio on Methanation Rate

CO in the inlet gas was kept constant and the total pressure in the reactor was varied. The results of these experiments are summarized in Figure 5, in which we have plotted the quotient of the methanation rate and the partial pressure of CO raised to the 0.46 power as a function of the partial pressure of H₂. Two pressure regimes were noted; one, with different reaction orders, the other with respect to be partial pressure of H₂. At low pressures of H₂ ($P_{H_2} < 5$ atm) the methana-

Table 2 Evaluation of Intrinsic Methanation Rate Constant

Temp (K)	P _{CO} (atm)	P _{H₂} (atm)	Methanation Rate (mol g ⁻¹ s ⁻¹) x 10 ⁶	Rate Constant (mol . g ⁻¹ . s ⁻¹) x 10 ⁶
523	4.8	35.4	27	17
	7.1	33.4	23	18
	10	30.3	20	19
543	2.7	25.0	80	46
	3.4	23.1	69	47
	2.1	24.5	86	45
	3.9	23.1	63	45
	3.5	22.9	68	47

tion rate is proportional to $P_{H_2}^1$. At high partial pressures of H_2 ($P_{H_2} > 7$ atm) the rate is proportional to $P_{H_2}^{0.53 \pm 0.04}$. The same behavior is exhibited at the two temperatures studied (Figure 5). For the high hydrogen-pressure regime we calculated the rate constant k for the methanation reaction

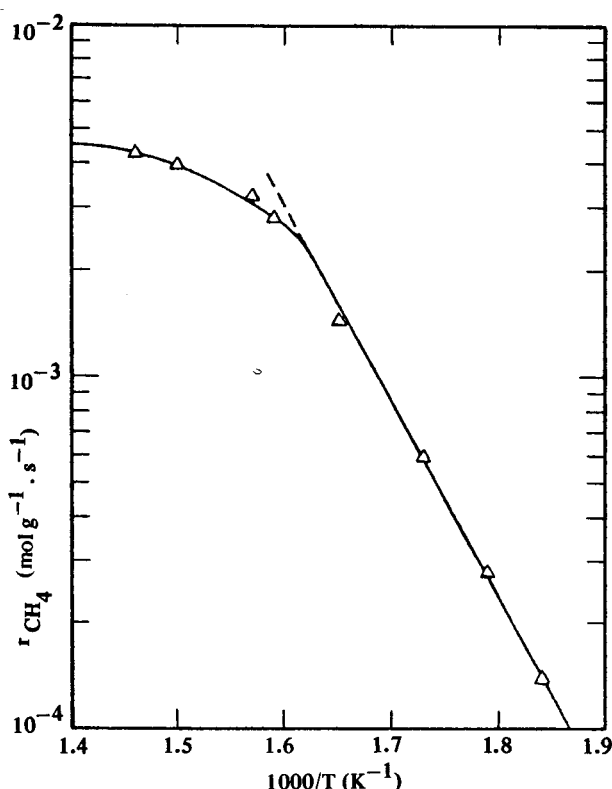


Figure 6. Variation in Methanation Rate with Temperature Total Pressure = 7.8 atm; $H_2/CO = 3$ by Vol).

(Table 2). From this data we calculated an activation energy of 27 kcal. mol⁻¹ for the methanation reaction.

A more precise value of the activation energy is obtained from the differential-reactor results (Figure 6). In these measurements the methanation rate was determined at low conversion over a wider range of temperatures. Only the data below 620 K exhibit chemical rate control under differential conditions (<12 vol% CO conversion). The resulting kinetic expression reads:

$$K = 1.5 \times 10^6 \exp(-25000/RT) \text{ mol. g}^{-1}\text{s}^{-1} \quad (1)$$

Above 620 K, corresponding to a methanation rate in excess of $3 \times 10^{-3} \text{ mol.g}^{-1} \text{ s}^{-1}$, the reaction rate deviated from the kinetic behavior prescribed by Equation (1). Because of mass transport limitations encountered at higher conversions, the methanation rate begins to fall off. These results establish the region in which transport parameters begin to govern the reaction kinetics.

3. Effect of Water

Since water is a major reaction product, a detailed assessment of its contribution to the methanation rate is important. Also, in the earlier phase of our study on catalyst selection^[1], the methanation activity of MCR-2X had been found to be affected by water in the feed.

Two types of experiments were performed with water added to the feed gas: one, under differential conditions in the fixed-bed reactor at a total pressure of one atmosphere, the other in the gradientless reactor at 34 atm.

The results clearly demonstrated a reduction in methanation rate caused by water. However, in each case the removal of water vapor from the feed stream restored the initial activity of the catalyst. The experimental data obtained in the presence of added water were examined, in terms of a parametric model based on a rate equation in the form:

$$r_{CH_4} = k P_{H_2}^x / (P_{CO}^y + c P_{H_2O}^z) \quad (2)$$

where r represents the methanation rate per gram of catalyst, k and c are empirical coefficients, and the exponents x , y , and z indicate the reaction orders with respect to H_2 , CO , and H_2O . From the results described in the preceding sections, the value of $x=1.0$ and $y = 0.46$ are the pressures used in these experiments. The coefficient c and the reaction

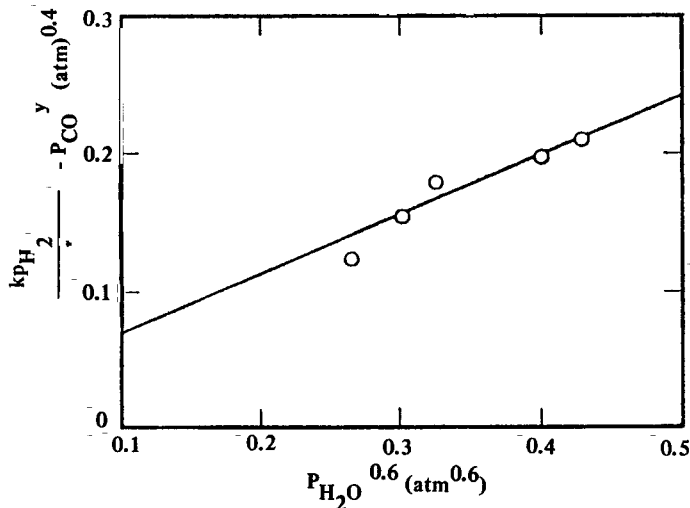


Figure 7. Evaluation of Reaction Order for Water Vapor in Rate Equation ($T = 573 \text{ K}$; $P_{H_2} = 0.75 \text{ atm}$; $P_{CO} = 0.25 \text{ atm}$; $GHSV = 1.3 \times 10^5 \text{ hr}^{-1}$)

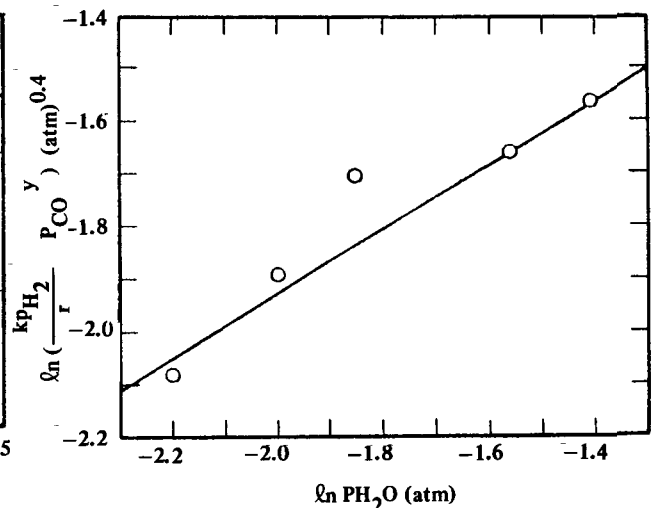


Figure 8. Evaluation of Coefficient C in Rate Equation ($T = 573 \text{ K}$; $P_{H_2} = 0.75 \text{ atm}$; $P_{CO} = 0.25 \text{ atm}$; $GHSV = 1.3 \times 10^5 \text{ hr}^{-1}$)

order z were determined from experimental measurements of the methanation rate in the presence of water at specified pressures of H_2 and CO .

By rearrangement of Equation (2) one obtains

$$\frac{kP_{H_2}}{r_{CH_4}} P_{CO}^{0.46} = cP_{H_2O}^z \quad (3)$$

thus the value of z can be determined by graphical analysis in a logarithmic plot of

the left hand side of Equation (3) versus $\ln P_{H_2O}$ (Figure 7). Similarly, the coefficient c is obtained by graphical analysis of the LHS of Equation (3) versus $P_{H_2O}^z$ (Figure 8). The exponent z is found to be 0.6 and the coefficient $c = 0.42 \text{ atm}^{-0.1}$.

Now we can proceed with an analysis of the methanation rate data derived from the Bertly reactor in the presence of added water vapor. In Table 3, the calculated rates of methanation based on Equation (4) are com-

Table 3 Effect of Water on Methanation Rate*

Reactor Mode	Gas Composition (atm)			Temperature (K)	Methanation Rate ($\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$) $\times 10^5$		
	CO	H_2	H_2O		exp.	cal.	
Differential*	0.25	0.75	0	573	27.5	27.5	
	0.22	0.66	0.12		19.8	20.6	
	0.20	0.59	0.21		17.2	17.4	
Gradientless	4.8	35.4	0.29	503	2.2	1.8	
	7.1	33.4	0.25		1.8	1.1	
	6.8	17.9	6.7		543	3.1	5.3
	3.9	19.5	2.8			6.3	7.8

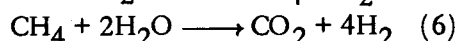
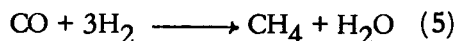
* $GHSV = 3 \times 10^5 \text{ hr}^{-1}$

pared with the experimental results for methanation in the fixed-bed and Bertly reactors over a range of total pressures and temperatures. In general, the agreement is quite satisfactory between the experimental results and the calculated values, indicative of the applicability of the empirical rate equation

$$r_{\text{CH}_4} = 1.5 \times 10^6 \exp(-26000/RT) \frac{1 \text{ (or 0.5)}}{P_{\text{H}_2}} / (P_{\text{CO}}^{0.46} + 0.42 P_{\text{H}_2\text{O}}^{0.6}) \quad (4)$$

4. Effect of CO₂

During methanation the production of CO₂ was observed in the fixed-bed and Bertly reactors. Its concentration appeared to be a nearly constant fraction of methane, even in the presence of water vapor added to the feed (Figure 9). This effect may result from steam reforming of methane under our experimental conditions. Thus the reaction sequence is given by the following two steps:



Surprisingly, the addition of CO₂ to the feed hardly affected the methanation rate, as shown by the results obtained in the fixed-bed reactor (Table 4). As a matter of fact, the data indicate that the carbon dioxide added to the feed in equimolar volume concentration with carbon monoxide did not undergo any conversion to methane.

Table 4 Effect of Carbon Dioxide on Methanation Rate*

He	Feed Gas (atm)		CO ₂	Production Rate	
	CO	H ₂		CH ₄ (mol · g ⁻¹ · s ⁻¹)	CO ₂ x 10 ⁴
0.16	0.21	0.63	0	2.66	0.11
0	0.20	0.60	0.20	2.66	0.10

* Experimental Conditions: Total Pressure = 1 atm; Temp = 573 K; GHSV = 3 x 10⁵ hr⁻¹

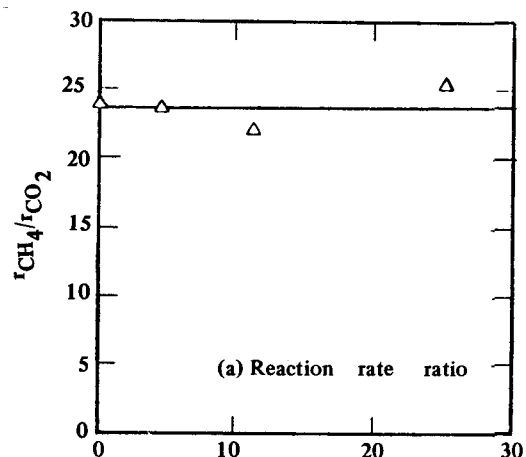


Figure 9. Effect of H₂O Vapor on CO₂ Formation

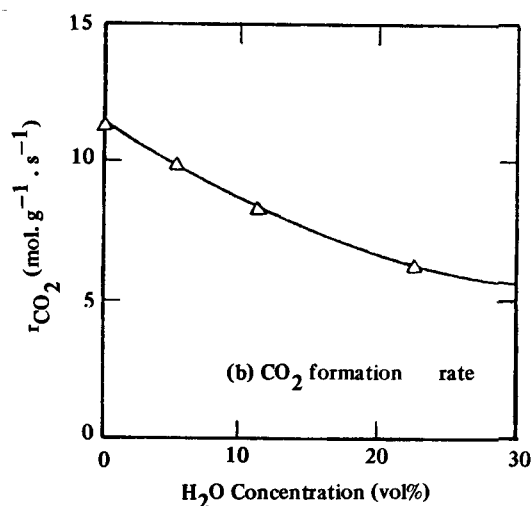


Figure 10. Catalyst Performance at High Temperature (H₂/CO = 3)

5. Catalyst Deactivation

In order to examine the suitability of MCR-2X for methanation/reforming at elevated

temperatures, several experiments were performed in a flow reactor at temperatures in excess of 750 K and a total pressure of 45 atm. Typical results are shown in Figure 10. It is to be noted that a significant loss in performance was observed at 787 K over a relatively short time period. Here we are showing the methanation activity normalized to its initial values. However, at 718 K and lower temperatures no significant decline in methanation was observed. Most likely the decline in the activity is not caused by morphological and structural changes, but rather by carbon deposition while operating with $H_2 / CO = 3$ at these elevated temperatures. Based on equilibrium calculations the phase boundary for graphite is approached under these conditions.

6. Catalyst Poisoning by Sulfur Compounds

One of the most serious problems in catalytic methanation is the deactivation of Ni-based catalysts by H_2S in the feed stream.

This process occurs at very low concentrations of H_2S (<0.1 ppm) under normal methanation conditions. The high sensitivity of the catalyst to sulfur poisoning is due to strong bonding between sulfur and metal surfaces. To obtain a measure of the sensitivity of MCR-2X to poisoning by hydrogen sulfide, we determined the intrinsic kinetic deactivation rate in the absence of mass transport limitations. An indication of the progressive loss in methanation rate under differential conditions (7 vol% CO conversion) is to be found in Figure 11. These data have been analyzed to provide a deactivation rate constant based on a model⁽²⁾ of first-order deactivation at low values of the Thiele modulus and high Reynolds numbers. At 600 K we obtain a deactivation rate constant of $k_d = 1.3 \times 10^{-4} \text{ sec}^{-1} \cdot \text{ppm}^{-1}$. This result compares to a value of $1.0 \times 10^{-4} \text{ s}^{-1} \cdot \text{ppm}^{-1}$ for another ni-based catalyst (Girdler G-65)[2].

After having established the value of k_d

Table 5 Heat and Mass Transfer Limitations During Catalytic Methanation

	Controlling Parameter	Analytical Criterion	Level Of Importance	Methanation Rate Ceiling* ($\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$)
MASS TRANSFER	EXTERNAL	HUDGINS ^(a)	INSIGNIFICANT	$r \gg 2 \times 10^{-4}$
	INTERNAL	WEISZ-PRATER ^(b)	SIGNIFICANT	$r > 10^{-3}$
HEAT TRANSFER	EXTERNAL	MEARS ^(c)	SIGNIFICANT	$r > 1.5 \times 10^{-2}$
	INTERNAL	ANDERSON ^(d)	SIGNIFICANT	$r > 6 \times 10^{-2}$

* Value above which transfer parameter begins to influence conversion.

(a) Hudgins, R. R. Can. J. Chem. Eng. 50, 427 (1972).

(b) Weisz, P. B., and Prater, C. D., Adv. Catal. 6, 143 (1954).

(c) Mears, D. E., J. Catal, 30, 283 (1973).

(d) Anderson, J. B., Chem. Eng. Sci. 18. 147 (1963).

at 600 K, we measured the rate of deactivation under similar conditions at 823 K. The results demonstrated a much faster rate of catalyst activity decay. Undoubtedly, this effect resulted from two processes, one caused by sulfur, the other by carbon. It will be recalled that, in this temperature range, carbon deactivation had been observed in the absence of sulfur (cf. Section 5).

7. Heat and Mass Transfer Consideration

For a catalytic exothermic reaction the intrinsic reaction kinetics are modified by the intrusion of external and internal mass- and heat- transfer phenomena. We have attempted to estimate the magnitude of these effects and their importance to the methanation process. In the analysis we used the following reaction conditions: catalyst temperature = 550 K; total pressure = 45 atm; $H_2/CO = 3$ (b. vol.), catalyst particle diameter = 0.1 cm. The results are summarized in Table 5. From these estimates we conclude that pore diffusion, as reflected by the magnitude of the internal mass transfer parameter, will be important under high pressure reaction conditions. Next, in line of importance, are the interparticle and intraparticle heat transfer processes which will begin to exert an influence on the rate of methane production at values greater by a factor of 100 than for the case of internal pore diffusion.

CONCLUSIONS

The results of this study demonstrate that catalyst MCR-2X exhibits many of the performance characteristics required by the local heat generation process, including high temperature stability, steam sintering resistance, and high methanation activity. The kinetics

of methane formation demonstrate inhibition by carbon monoxide and steam. The reaction order with respect to hydrogen is dependent on the absolute pressure in the reactor. At pressures above 7 atm the rate is proportional to $P_{H_2}^{1/2}$ at lower pressure to P_{H_2} . With increasing temperature, the methanation rate becomes mass-transport limited. For example at $H_2/CO = 3$, $P_t = 7.8$ atm., we observe a transition from reaction-kinetics control to mass-transport control at 620 K and a methanation rate of $3 \times 10^{-3} \text{ mol. g}^{-1} \text{ s}^{-1}$.

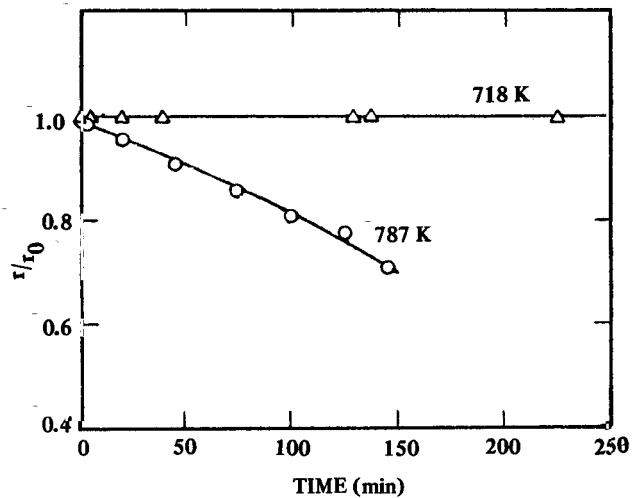


Figure 11. Effect of Hydrogen Sulfide (4.5 ppm) in Feed Gas on Methanation Activity in Differential Reactor ($P_{H_2} = 5.9$ atm; $P_{CO} = 1.9$ atm; $T = 599$ K; $GHSV = 4.2 \times 10^5 \text{ hr}^{-1}$)

Under our experimental conditions neither CH_4 nor CO_2 made a contribution to the methanation rate. A similar observation was made in another study with Ni-based catalyst on various support materials in a fluidized bed. For Ni on $MgAl_2O_4$ spinel the published data on methanation kinetics bear some resemblance to ours. For example, the overall activation energy is reported to be $E = 23.4 \text{ Kcal. mol}^{-1}$; the reaction order with respect to H_2 is given as 0.5, and with respect to CO as -0.5 , in line with our results. However

Schoubye^[3] did not investigate the effect of water on methanation rate. Our data clearly indicate its retarding influence, probably associated with steam reforming of methane under synthesis conditions.

As expected, the catalyst is deactivated by hydrogen sulfide. The deactivation rate observed is similar to that encountered with other Ni-based catalysts. Based on the measured deactivation rate constants, the catalyst life may be estimated in the presence of sulfur impurities at different levels in the feed.

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