Reaction Kinetics for the Synthesis of Methanol from CO and H₂ on a Copper Catalyst

Reaktionskinetik der Methanolsynthese aus CO und H₂ auf einem Kupferkatalysator

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Abstract

The kinetics for the low-pressure synthesis of methanol from CO and H₂ were studied in a small integral reactor. The mole fraction of CO was varied from 0.1 to 0.54, the total pressure from 3 to 9 MPa and the temperature from 483 to 545 K.

Using the maximum likelihood approach, seventeen possible reaction rate correlations were evaluated statistically. Among these models three appear to fit the experimental data satisfactorily.

Kurzfassung

Kinetische Untersuchungen der Methanolsynthese aus CO und H₂ mit einem Niederdruckkatalysator wurden in einem kleinen, integralen Versuchsreaktor durchgeführt. Die Molfraktion des Kohlenmonoxids im Synthesegas, der Totaldruck und die Temperatur wurden entsprechend von 0.1 bis 0.54, von 3 bis 9 MPa und von 483 bis 545 K variiert.

Siebzehn verschiedene Reaktionsgeschwindigkeitsansätze wurden einer auf dem 'Maximum Likelihood Prinzip' gründenden statistischen Auswertung unterworfen. Drei Ansätze ergaben eine befriedigende Übereinstimmung mit den Meßdaten.

Synopse

Die katalytische Hydrierung des Kohlenmonoxids ist heute der wichtigste Produktionsweg zum Methanol [1]. Trotz der scheinbaren Simplizität der mit Gl. (1) vorgestellten Reaktion ergaben bisherige Studien [2–15] kein eindeutiges mechanistisches Bild dieser Reaktion (Tab. 1). Durchführung genauer Messungen und Verarbeitung der Meßdaten werden durch die drastischen Reaktionsbedingungen, das stark exotherme Verhalten der Reaktion, sowie durch das Auftreten verschiedener Nebenreaktionen (Gl. (2)–(6)) bedeutend erschwert. In der vorliegenden Arbeit beabsichtigten wir eine adäquate kinetische Korrelation für die Reaktion (1) auf dem BASF S3-85 Niederdruckkatalysator zu finden. Auch die Lebensdauer des Katalysators in Abwesenheit des Kohlendioxids im Synthesegas sollte festgestellt werden.

Das Meßsystem ist auf Abb. 1 gezeigt. Ein Festbettreaktor von integralem Typ wurde wegen seines besonders einfachen Aufbaus gewählt. Der $10 \times 10^{-6} \text{ m}^3$ Reaktor hat einen Durchmesser von $8 \times 10^{-3} \text{ m}$ und ist mit einem elektrischen Ofen sowie mit einem massiven

Bronzeblock zum Temperatenausgleich ausgestattet (Abb. 2(a)). Das Katalysator-Festbett besteht aus $(0.7\text{--}1.2) \times 10^{-3} \text{ m}$ Katalysator-Splintern die mit zermahlenem Alumina-Träger vermischt sind, so daß die Katalysatorbett-Länge $40 \times 10^{-3} \text{ m}$ beträgt. Der Totaldruck wird mit einem Druckregler eingestellt. Die Stabilität und Homogenität der Temperatur wird mit fünf kalibrierten Thermoelementen kontrolliert. Die Temperaturregelung erfolgt automatisch mit Hilfe eines Hewlett-Packard 9826 PC. Kalibrierte CO/H₂ Mischungen werden dem Reaktor aus einer Batterie von Hochdruck-Zylindern zugeführt. Der Gasdurchsatz wird mit zwei Präzisionsventilen am Reaktorausgang geregelt und mittels einer Gasuhr gemessen. Die Analyse der Gasgemische am Eingang sowie am Ausgang des Reaktors erfolgt gaschromatografisch mit Hilfe eines Wärmeleitfähigkeitsdetektors. Als Trägergas wird Wasserstoff verwendet.

Vor der Inbetriebnahme wird der Katalysator mit N₂/H₂-Gemischen – bei steigendem Molenbruch von Wasserstoff unter 0.4 MPa und bei 443–523 K langsam reduziert. Nach 3-tägiger Formierung stabilisiert sich die Aktivität des Katalysatormusters. Eine Messung

beginnt mit der Einstellung der gewünschten Temperatur, des Totaldruckes und der Gasbelastung. Nach der 2 bis 6 Stunden dauernden Stabilisierung werden der Gasdurchsatz am Reaktorausgang, die Zusammensetzung des Produktgases und das axiale Temperaturprofil im Festbett bestimmt und können die gewünschten Werte zu einem neuen Meßpunkt eingestellt werden. Zur Kontrolle der Aktivität des Katalysators wurden mehrmals Standardmessungen wiederholt.

Es wurde festgestellt, daß die Nebenreaktionen nach Gl. (5) und/oder (6) bei niedrigen Gasdurchsätzen nicht vernachlässigbar sind. Bei hohen Partialdrücken von Dimethylläther verliert der Katalysator seine Aktivität innerhalb von einigen Tagen. Eine sehr schnelle (innerhalb von 2 Stunden) und vollständige Degradation wurde auch bei sehr hohen Molenbrüchen von CO von etwa 0.90 im Synthesegas festgestellt.

Insgesamt wurden 110 Messungen im Versuchsreaktor durchgeführt (Tab. 4). Da die Reaktion stark exotherm verläuft ($\Delta H_{298} = -91 \text{ kJ mol}^{-1}$), konnte das Katalysator-Festbett nicht exakt isotherm gehalten werden: in der Reaktorachse wurden Temperaturunterschiede bis zu 3 K gemessen. Zu weiteren Berechnungen wurde ein mittlerer Wert nach Gl. (7) verwendet.

Der Berechnung experimenteller CO-Umsatzungsgrade ζ_{CO} liegt Gl. (8) zugrunde. Die Stoffbilanz bezüglich des Kohlenstoffs wird mit Gl. (9) kontrolliert. Der Gasdurchsatz am Reaktorausgang folgt aus Gl. (10) und die 'Kontaktzeit' τ wird mit Gl. (11) berechnet. Auf Abb. 3 sind typische Meßdaten gezeigt. Aus einer Fehlerbetrachtung folgte die Schlußfolgerung, daß die wesentlichen Fehler der Messungen auf die Temperaturgradienten im Katalysatorbett zurückgehen. Es ist aber auch zweifelhaft, ob man durch den Einsatz eines Differentialreaktors mit innerem Kreislauf die Temperaturmeßfehler vollständig beseitigen kann [10, 12, 13, 15]. Die Meßfehler werden teilweise auch dem promovierenden Einfluß des nach Gl. (2), (5) und/oder (6) geildeten Wassers auf die Aktivität des Katalysators [7] zugeschrieben.

Die 17 Langmuir-Hinshelwood und Eley-Rideal Reaktionsmodelle (Tab. 3) wurden einer statistischen Auswertung unterworfen. Dazu wurde das RKPEs Program herangezogen, das von Klaus und Rippin [19] entworfen wurde. Der Berechnung des CO-Umsatzes liegt Gl. (12) zugrunde, wobei die spezifische Reaktionsgeschwindigkeit R_{CO} eine Funktion der Temperatur und der Fugazitäten von den Reaktionskomponenten ist. Diese Fugazitäten ϕ_i werden mit Gl. (13) berechnet, wobei die Molfraktionen y_i aus Gl. (14)–(16) folgen. Die Fugazitätskoeffizienten f_i ergeben sich aus den von Peng und Robinson [20] gegebenen Gl. (17)–(18). Die Gleichgewichtskonstante der Reaktion (1) folgt aus Gl. (19). Mit Hilfe des RKPEs-Programms wurden die optimalen Werte der kinetischen Parametern in den 17 Ansätzen berechnet. Zur Auswahl der adäquaten Ansätze wurden drei Faktoren beachtet:

(1) Summe der Abstandsquadrate;

(2) T-Parameter (Quotient der Parameter-Werte und ihrer Standardabweichungen);

(3) Symmetrie der Verteilung der Abweichungen.

Drei der geprüften Ansätze (Nr. 1, 4 und 12 in Tab.

3) ergeben eine gute Übereinstimmung mit den Meßdaten (Tab. 6). Auf Abb. (4) wird die Verteilung der Abweichungen für diese Ansätze gezeigt. Abbildung 5 demonstriert dagegen eine nicht-symmetrische Verteilung eines verworfenen Ansatzes. Ansatz 1 wurde auch von anderen Autoren [2, 13] gefunden. Wegen der niedrigen T-Werte können wir bezüglich der möglichen Reaktionsmechanismen keine Schlußfolgerungen ziehen.

Zur Berechnung der Reaktionsgeschwindigkeit R_{CO} kann man entweder Gl. (20) oder Gl. (21) gebrauchen. Die von uns gefundenen Reaktionsgeschwindigkeiten sind um etwa einen Faktor 6 niedriger als diejenige von Seyfert und Luft [12] für denselben Katalysator festgestellten. Dieser Unterschied ist primär durch die Abwesenheit des Kohlendioxids in unseren Synthesegasen bedingt. Auch ohne CO_2 behält der BASF S3-85 Methanolkontakt monatenlang seine Aktivität und Selektivität. Das Auftreten von Nebenreaktionen und die Fehler der Temperaturmessungen verursachen die relativ großen Meßfehler im Integralreaktor.

Introduction

The catalytic hydrogenation of carbon monoxide is nowadays the most important route to methanol production. In spite of its apparent simplicity, experimental studies of the reaction

hitherto did not result in an unequivocal mechanistic reaction model, possibly due to experimental and interpretational problems. Modern catalysts require temperatures of at least 473 K and consequently the use of high total pressures, for example, from 4 to 20 MPa, in order to overcome the thermodynamic limitations. These conditions, together with the high exothermicity of reaction (1) ($\Delta H_{298} = -91 \text{ kJ mol}^{-1}$, which results in an adiabatic temperature rise of around 1000 K for a stoichiometric reaction mixture) and the possible parallel and consecutive reactions, cause significant difficulties, both in the experiments and in the elaboration of the data obtained.

Reaction (1) can be accompanied by several side and consecutive reactions; examples are [1]:

and

or

Whether these reactions cause significant reactant losses depends on the catalyst and on the operating conditions used. Generally, the modern copper catalysts are highly selective.

We needed quantitative information on the kinetics of reaction (1) using the BASF S3-85 catalyst and CO₂-free synthesis gas. Our main objectives were (1) to obtain a reliable kinetic correlation for the operating conditions mentioned, and (2) to examine whether the copper catalyst functions well in the absence of CO₂. For our kinetic measurements we chose the integral, packed tubular reactor in view of its simplicity of construction, especially for experiments at high temperatures and pressures.

Literature survey

A first comprehensive discussion of the kinetics of the methanol synthesis reaction was published by Natta *et al.* in 1953 [2]. Since then the number of papers published concerning the methanol synthesis reaction has been increasing gradually. Although the reaction mechanism is not fully understood, nevertheless much progress has been made in the last two decades in improving the properties of the catalysts. The catalysts based on ZnO were replaced by the highly active Cu/ZnO catalysts: this allowed a reduction of the reaction pressures from 20–30 MPa to 5–10 MPa and of the reaction temperature by about 50 K, down to 500–550 K.

In the studies published a large variety of catalysts, feed gas compositions and operating conditions was used; regretfully, it is not possible to draw general conclusions from them on the reaction mechanism. Furthermore, it is not known whether the reaction mechanisms for the ZnO/Cr₂O₃ and for the Cu/ZnO catalysts are identical or not. Denny and Whan [3], Kung [4] and Klier and co-workers [5–7] summarized and extensively discussed the findings on the mechanism of the methanol synthesis reaction. Generally, the main reaction (1) is considered to proceed in a series of steps involving adsorption of the reactants, chemical reactions of a Langmuir–Hinshelwood or an Eley–Rideal type, and product desorption.

Depending on the rate determining step, a large number of kinetic expressions has been proposed in the literature. In Table 1 the postulated reaction rate

TABLE 2. Possible reaction mechanisms [8]

No.	Mechanism
1	$\text{CO}^* + 2\text{H}_2^* = \text{CH}_3\text{OH}^* + 2\text{S}$
2	$\text{CO}^* + 2\text{H}_2 = \text{CH}_3\text{OH}^*$
3	$\text{CO} + 2\text{H}_2^* = \text{CH}_3\text{OH}^* + \text{S}$
4	$\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$
5	$\text{CO} + \text{H}_2 = \text{HCHO}$
	$\text{HCHO} + \text{H}_2 = \text{CH}_3\text{OH}$

* indicates component in adsorbed state; S is an adsorption site.

TABLE 1. The most important kinetic expressions for the methanol synthesis reaction

Catalyst	Pressure (MPa)	Temperature (K)	Rate expression	Ref.
ZnO/Cr ₂ O ₃	20–30	573–673	$\frac{k(\phi_{\text{CO}}\phi_{\text{H}_2}^2 - \phi_{\text{M}}/K_{\text{eq}})}{(1 + A\phi_{\text{CO}} + B\phi_{\text{H}_2} + C\phi_{\text{M}})^3}$	[1, 8]
ZnO/Cr ₂ O ₃	20–30	573–673	$\frac{k(\phi_{\text{CO}}\phi_{\text{H}_2}^2 - \phi_{\text{M}}/K_{\text{eq}})}{\phi_{\text{H}_2}(1 + A\phi_{\text{CO}} + B\phi_{\text{M}}/\phi_{\text{CO}} + C\phi_{\text{M}} + D\phi_{\text{H}_2})^2}$	[8]
			$\frac{k(\phi_{\text{CO}}\phi_{\text{H}_2}^2 - \phi_{\text{M}}/K_{\text{eq}})}{(1 + A\phi_{\text{CO}} + B\phi_{\text{H}_2} + C\phi_{\text{CO}}\phi_{\text{H}_2} + D\phi_{\text{M}})^2}$	
Cu/ZnO/Al ₂ O ₃	4–6	493–533	$k \left(\frac{P_{\text{CO}}^{0.5} P_{\text{H}_2}}{P_{\text{M}}^{0.66}} - \frac{P_{\text{M}}}{P_{\text{CO}}^{0.5} P_{\text{H}_2} K_{\text{eq}}} \right)$	[9]
Cu/ZnO/Al ₂ O ₃	2–8	483–538	$\frac{k(\phi_{\text{CO}}\phi_{\text{H}_2}^2 - \phi_{\text{M}}/K_{\text{eq}})}{(1 + A\phi_{\text{CO}} + B\phi_{\text{H}_2} + C\phi_{\text{M}} + D\phi_{\text{CO}_2})^2}$	[10]
ZnO/Cr ₂ O ₃	5	473–573	$k \left(\frac{P_{\text{CO}}^{0.25} P_{\text{H}_2}}{P_{\text{M}}^{0.25}} - \frac{P_{\text{M}}^{0.25}}{P_{\text{CO}}^{0.25} K_{\text{eq}}} \right)$	[11]
Cu/ZnO/Al ₂ O ₃	8–14	503–538	$\frac{k(\phi_{\text{CO}}\phi_{\text{H}_2}^2 - \phi_{\text{M}}/K_{\text{eq}})}{(1 + A\phi_{\text{CO}} + B\phi_{\text{H}_2} + C\phi_{\text{M}} + D\phi_{\text{CO}}\phi_{\text{H}_2}^2 + E\phi_{\text{CO}_2})^2}$	[12]
Cu/ZnO/Al ₂ O ₃	3–9.4	488–523	$\frac{k(\phi_{\text{CO}}\phi_{\text{H}_2}^2 - \phi_{\text{M}}/K_{\text{eq}})}{(1 + A\phi_{\text{CO}} + B\phi_{\text{CO}_2} + C\phi_{\text{H}_2})^3}$	[13]
Cu/ZnO/Al ₂ O ₃	3.1–5.2	493–545	$k P_{\text{CO}}^{0.5} P_{\text{H}_2}^2 \left(1 - \frac{P_{\text{M}}}{P_{\text{CO}} P_{\text{H}_2}^2 K_{\text{eq}}} \right)$	[14]

TABLE 3. Kinetic expressions for the methanol synthesis reaction [8]

Model No.	Reaction mechanism (see Table 2)	Rate determining step	Rate expression R_{CO}
1	1	$CO^* + 2H_2^* = CH_3OH^* + 2S$	$\frac{k(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})}{(1 + A\phi_{CO} + B\phi_{H_2} + C\phi_M)^3}$
2	1	$CH_3OH^* = CH_3OH + S$	$\frac{k(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})}{1 + A\phi_{CO} + B\phi_{H_2} + C\phi_{CO}\phi_{H_2}^2}$
3	2	$CO^* + 2H_2 = CH_3OH^*$	$\frac{k(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})}{1 + A\phi_{CO} + B\phi_M}$
4	2	$CH_3OH^* = CH_3OH + S$	$\frac{k(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})}{1 + A\phi_{CO} + B\phi_{CO}\phi_{H_2}^2}$
5	3	$CO + 2H_2^* = CH_3OH^* + S$	$\frac{k(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})}{(1 + A\phi_{H_2} + B\phi_M)^2}$
6	4	$CO + 2H_2 = CH_3OH$	$k(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})$
	5	$HCHO + H_2 = CH_3OH$	$k(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})$
7	5	$CO^* + H_2^* = HCHO^* + S$	$\frac{k(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})}{\phi_{H_2}(1 + A\phi_{CO} + B\phi_M/\phi_{H_2} + C\phi_M + D\phi_{H_2})^2}$
8	5	$HCHO^* + H_2^* = CH_3OH^* + S$	$\frac{k(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})}{(1 + A\phi_{CO} + B\phi_{H_2} + C\phi_M + D\phi_{CO}\phi_{H_2})^2}$
9	5	$CO + S = CO^*$	$\frac{K(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})}{\phi_{H_2}^2(1 + A\phi_M/\phi_{H_2}^2 + B\phi_M/\phi_{H_2} + C\phi_M + D\phi_{H_2})}$
10	5	$H_2 + S = H_2^*$	$\frac{k(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})}{\phi_{CO}\phi_{H_2}[1 + A\phi_{CO} + B(\phi_M/\phi_{CO})^{0.5} + C\phi_M/\phi_{H_2} + D\phi_M]}$
11	5	$CH_3OH^* = CH_3OH + S$	$\frac{k(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})}{\phi_{H_2}(1 + A\phi_{CO} + B\phi_{H_2} + C\phi_{CO}\phi_{H_2} + D\phi_{CO}\phi_{H_2}^2)}$
12	5	$CO + H_2 = HCHO$	$\frac{k(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})}{\phi_{H_2}}$
13	1	$CO + S = CO^*$	$\frac{k(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})}{\phi_{H_2}^2(1 + A\phi_{H_2} + B\phi_M/\phi_{H_2} + C\phi_M)}$
14	1	$H_2 + S = H_2^*$	$\frac{k[\phi_{H_2} - \phi_M^{0.5}/(\phi_{CO}K_{eq})^{0.5}]}{1 + A\phi_{CO} + B(\phi_M/\phi_{H_2})^{0.5} + C\phi_M}$
15	2	$CO + S = CO^*$	$\frac{k(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})}{\phi_{H_2}^2(1 + A\phi_M\phi_{H_2}^2 + B\phi_M)}$
16	3	$H_2 + S = H_2^*$	$\frac{k[\phi_{H_2} - \phi_M^{0.5}/(\phi_{CO}K_{eq})^{0.5}]}{1 + A(\phi_M/\phi_{CO})^{0.5} + B\phi_M}$
17	3	$CH_3OH^* = CH_3OH + S$	$\frac{k(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})}{1 + A\phi_{H_2} + B\phi_{CO}\phi_{H_2}^2}$

expressions are summarized. Many experimental studies were carried out under conditions where the main reaction (1) proceeds only in the forward or in the backward direction: the synthesis at very low methanol concentrations or the decomposition of methanol at atmospheric pressure. Kinetic expressions obtained in these studies are not listed in our Table 1 because in practical situations the effective methanol production rate is affected considerably by the reversed reaction, so that the kinetics of the decomposition reaction must also be taken into account. Furthermore, the studies of the decomposition reaction were carried out almost in the absence of CO and H₂, whereas these components may significantly affect the chemisorption of methanol on the catalyst surface. Even more kinetic expressions have been proposed by Buzzi Ferraris and Donati [8]; assuming the Langmuir-Hinshelwood or Eley-Rideal type of mechanisms of Table 2 and taking various steps as rate determining, they derived the 17 kinetic expressions listed in Table 3. Recently most authors have proposed that reaction (1) is of Langmuir-Hinshelwood or Eley-Rideal type [7, 12, 13]. Seyfert and Luft [12] probably published the most extensive experimental study using the BASF S3-85 catalyst and a CO₂-containing synthesis gas. Their measurements were carried out in a recycle jet-loop reactor. Owing to high temperatures and total pressures (Table 1) and low partial pressures of methanol, very high reaction rates were measured. After a statistical elaboration they proposed expression 8 of Table 3, which is based on the hypothesis of a bimolecular surface reaction involving an adsorbed intermediate. Villa *et al.* [13], in a Bertly reactor, studied the methanol synthesis reaction over a Cu/ZnO/Al₂O₃ catalyst and used

CO₂-containing synthesis gas. They obtained a good fit of the experimental data using expression 1 from Table 3, which was originally proposed by Natta *et al.* [2] and recently partially confirmed by Klier *et al.* [7].

Experimental part

The experimental set-up

The experimental installation is shown diagrammatically in Fig. 1. A stainless steel tubular reactor with an inner diameter of 8×10^{-3} m and a volume of 10×10^{-6} m³ was inserted in a massive cylindrical bronze block to ensure the isothermicity of the reactor wall. The block was surrounded by an electric heating oven. The constructional details of the reactor are shown in Fig. 2(a). A catalyst sample of about 1.5×10^{-3} kg consisting of crushed catalyst particles of size $(0.7-1.2) \times 10^{-3}$ m mixed with crushed alumina was placed in the reactor tube. The length of the catalyst bed was 40×10^{-3} m. The catalyst bed was located in the middle of the reactor tube, where the axial temperature gradients are negligible in the case of no reaction (see Fig. 2(b)). The remainder of the reactor tube in front of and behind the catalyst bed was filled with crushed particles of alumina. A Bourdon-type precision gauge was installed at the reactor inlet to determine the total pressure. This pressure was adjusted by means of a manually controlled precision pressure regulator which was also installed at the reactor inlet. The reactor temperature was measured using five calibrated type K thermocouples. Two of them, with a diameter of 0.5 mm, were used for the determination of the axial temperature profile

Fig. 1. The experimental set-up: 1, feed gas bottles; 2, needle valve; 3, precision valve; 4, pressure regulators; 5, thermocouple; 6, reactor tube; 7, bronze block; 8, heating oven; 9, catalyst bed; 10, inert packing; 11, thermocouple sheaths; 12, heating element; 13, expansion valves; 14, cold-trap vessel; 15, rotameter; P, pressure gauge; PC, personal computer and interface; F, gas meter; GC, sampling point for chromatographic analysis; TR, temperature controller.

Fig. 2. (a) Construction details of the reactor: 1, gas inlet; 2, gas outlet; 3, reactor tube; 4, bronze block; 5, heating oven; 6, insulation; 7, support grid; 8, inert packing; 9, catalyst bed; 10, thermocouple sheaths; 11–13, thermocouples. (b) Typical temperature profiles measured along the reactor axis: curve a, without, and b, with reaction; experiment No. 72 (Table 4).

along the reactor wall and reactor axis, respectively. These thermocouples were installed in stainless steel sheaths (outer diameter 1.6 mm) in such a way that the position of the thermocouple welds can be changed easily. The other three thermocouples, with a diameter of 1.6 mm, were installed at both ends of the reactor or in the bronze block. An additional thermocouple, installed in the heating oven (see Fig. 2(a)), was connected to the Eurotherm type 810 temperature controller. A Hewlett-Packard 9826 personal computer equipped with an HP 3497A data acquisition/control unit was used to measure the reactor temperatures.

The set point of the temperature controller of the heating oven was also adjusted by the computer. Based on readings from the 0.5 mm thermocouple installed in the sheath at the outer reactor wall, the computer corrects the set point until the desired wall temperature of the reactor is reached. At this stage the thermocouple weld is positioned in the middle of the reactor length. The temperature of the reactor wall can be kept constant with a reproducibility of ± 0.05 K, being practically free of fluctuations.

The feed gas was supplied from gas bottles filled with CO/H₂ mixtures. The composition of these mixtures was checked frequently. The composition of feed and product gas was determined with a Varian model 3770 gas chromatograph equipped with a thermal conductivity detector and a 1.5 m long, 1/8 in. diameter Porapak-Q column. In order to facilitate the on-line gas analysis the gas chromatograph was

equipped with a Hewlett-Packard 3390A programmable integrator and with a peristaltic sampling pump coupled to a pneumatic sampling valve. Hydrogen was used as carrier gas. The detector was found to be linear for CO and CH₃OH as well as for dimethyl ether and water. The gas stream leaving the reactor was expanded to atmospheric pressure over two needle valves; these were also used for flow adjustment. The valves were heated externally so that methanol condensation was prevented. The low-pressure piping for the product gas was at room temperature. In most experiments the mole fraction in the product gas of methanol was 0.1 or lower, so that the methanol could not condense. To prevent condensation of methanol in the downstream piping behind the expansion valves, a small cold-trap vessel was installed. If necessary, the methanol production was determined as the sum of the rate of condensation in the cold-trap vessel plus the rate of carry-away in the outlet gas flow. The outlet gas flow was determined with a wet gas meter. A rotameter was also installed at the gas outlet to be used for flow adjustment.

The experimental procedure

After filling the reactor, leak tests were carried out using pure hydrogen at 15 MPa. Then the catalyst was activated by reduction: to this end it was rinsed with H₂/N₂ mixtures starting with a hydrogen content of 1 vol.% at a temperature of 443 K and a total pres-

sure of 0.4 MPa. After one hour both the temperature and the hydrogen content were gradually increased up to 523 K and 20 vol.% H_2 respectively over a period of 12 hours. The reactor effluent at the end of the reduction was free of water vapour. After reduction of the catalyst, it was treated with a continuous stream of 20/80 vol.% of CO/H_2 at 523 K and 6 MPa to stabilize the catalyst activity. We found a period of 72 hours to be sufficient for stabilization of the catalyst; for a CO_2 -containing synthesis gas Seyfert and Luft [12] suggest a period of 96 hours. The leak tests and the activation procedures were repeated after every new filling of the reactor with fresh catalyst.

An experiment was started by first setting the desired pressure and temperature. Then the gas flow was adjusted with the needle valves and the rotameter at the reactor outlet. The feed gas flow cannot be determined directly, therefore it was calculated after completion of an experiment. Depending on the operating conditions chosen, the reactor reached a steady state after 2–6 hours. Then the product gas flow, the product gas composition and the axial temperature profile were determined. After this, the conditions for a subsequent experiment can be adjusted. In between the experiments, the catalyst was kept at 0.2 MPa and at around 500 K in a mixture of nitrogen and hydrogen of 20/80 vol.%. The catalyst activity was checked frequently by executing a standard experiment.

Concerning the intraparticle mass transfer resistances, we refer to Seyfert and Luft [12], who for the same BASF S3-85 catalyst determined the reaction rates at varying particle diameters. They found that for crushed catalyst particles of diameter 1 mm the effectiveness factor equals unity. Since our measurements were carried out at much less severe conditions (on average our reaction rates were about 5–15 times lower), we assume the intraparticle transfer resistances to be absent.

Catalyst stability

We observed that reactions (5) and/or (6) become significant for experiments at low feed flows, where the conversions approach the actual equilibrium for reaction (1) and the mole fractions of water or dimethyl ether exceed 1 vol.%. At high dimethyl ether contents we observed a relatively quick and irreversible loss of catalyst activity within several days of operation. The deactivated catalyst particles were violet in colour and had lost their mechanical strength. Also, scanning electron microscope photographs showed changes in the texture of the catalyst surface. Several simple batch experiments, in which samples of fresh catalyst were kept in an atmosphere of dimethyl ether, confirmed our assumption that this compound causes a degradation of the catalyst. Another unexpected degradation was observed during experiments with high CO partial pressures, using a synthesis gas containing 90 vol.% CO and 10 vol.% H_2 : the catalyst activity was completely lost in less than two hours.

We have no explanation for either of these types of degradation. Possibly they only occur if there is no CO_2 present in the synthesis gas.

Results

A total of 110 experiments were carried out at various temperatures, pressures, feed gas compositions and flow rates. The experimental conditions and the results are specified in Table 4; they are arranged in groups of data with equal feed gas composition. As already mentioned, owing to the exothermicity of the reaction, the temperature in the catalyst bed was not uniform; an example of a temperature profile measured along the reactor axis is shown in Fig. 2(b). For the experiments of Table 4, the temperature differences measured along the catalyst bed never exceeded 3 K, whereas in about 90% of the cases these differences were lower than 2 K. The temperatures reported in Table 4 are mean values: the axial temperature was measured at 5 mm intervals along the 40 mm bed (see Fig. 2(b)), the mean value being calculated by

$$\bar{T} = \frac{1}{9} \sum_{i=1}^9 T_i \quad (7)$$

The temperature measured at the outside of the reactor wall was always practically constant over the whole bed length. In all experiments the concentrations of both dimethyl ether and water, being the products of the most important undesired reactions (5) and/or (6), were always considerably below 1 vol.%, so that their quantitative determination was very inaccurate. We decided in calculating conversions to abstain from correcting for the formation of side products so that the conversion ζ_A was calculated from the measured mole fractions of CO at the inlet and the outlet of the reactor according to

$$\zeta_{CO} = \frac{y_{CO, in} - y_{CO, out}}{y_{CO, in} - 2y_{CO, out}y_{CO, in}} \quad (8)$$

The carbon balance was checked with

$$y_{M, out} = \frac{\zeta_{CO}}{1 - \zeta_{CO}} y_{CO, out} \quad (9)$$

For all experiments, the carbon balance holds to an accuracy of better than 5%. The molar feed flow of CO follows from

$$\Phi_{CO, in} = \frac{\Phi_{CO, out}}{1 - \zeta_{CO}} \quad (10)$$

and the 'contact time' τ from

$$\tau = \frac{m_{cat}}{\Phi_{CO, in}} \frac{\text{kg cat s}}{\text{mol CO in}} \quad (11)$$

In Fig. 3, typical conversion versus 'contact time' data are presented.

To check for interparticle mass transfer resistances several experiments reported in Table 4 were carried out with feed gas flows and amounts of catalyst increased by a factor of 2.5, so that the 'contact time' τ

TABLE 4. Experimental data

Expt. No.	P_T (MPa)	$y_{CO, in}$	T (K)	τ ($\frac{kg\ cat\ s}{mol\ CO}$)	ζ_{CO}	Expt. No.	P_T (MPa)	$y_{CO, in}$	T (K)	τ ($\frac{kg\ cat\ s}{mol\ CO}$)	ζ_{CO}
1	4.03	0.102	522.0	79.2	0.036	59	3.10	0.382	513.8	16.2	0.020
2	4.04		522.2	88.6	0.050	60	3.10		513.9	27.1	0.018
3	4.01		522.5	94.7	0.047	61	3.10		513.1	55.4	0.032
4	4.05		522.2	108.5	0.032	62*	3.13		513.5	57.6	0.033
5	4.05		521.4	123.8	0.077	63	3.11		512.9	60.5	0.043
6	4.01		522.1	137.8	0.085	64	3.10		513.4	92.9	0.060
7	4.04		521.4	142.3	0.091	65	3.10		514.0	103.6	0.063
8	4.02		522.2	173.2	0.128						
9	4.05		520.6	189.0	0.133	66	3.11	0.382	534.4	56.3	0.058
10*	4.06		521.9	230.0	0.193	67	3.09		535.8	118.6	0.100
11	4.08		522.6	264.6	0.177	68	3.09		535.8	118.8	0.098
12	4.03		522.2	169.2	0.223						
13	4.05		520.9	279.4	0.228	69	3.10	0.382	542.6	7.8	0.017
14	4.06		522.3	295.2	0.284	70	3.07		542.2	25.7	0.057
15	4.02		521.8	343.1	0.283	71	3.10		543.6	30.0	0.049
16	4.03		522.3	447.5	0.413	72	3.10		543.6	35.9	0.058
17	4.05		521.9	476.8	0.397	73	3.07		543.5	39.2	0.076
18	4.05		522.5	483.1	0.427	74*	3.08		544.6	46.1	0.085
19	4.05		522.3	615.2	0.509	75	3.09		545.4	51.9	0.087
20	4.05		520.6	1103.4	0.545	76	3.10		542.8	58.5	0.104
21	4.06		521.1	1211.4	0.583	77	3.10		546.0	61.6	0.107
						78	3.10		544.8	82.2	0.113
22	5.04	0.102	520.9	95.4	0.061	79	3.10		543.9	87.3	0.114
23	5.02		520.8	175.1	0.190	80	3.10		545.5	88.0	0.124
24	5.06		521.1	177.4	0.177						
25	5.04		520.9	203.1	0.198	81	5.07	0.382	514.6	30.8	0.015
26*	5.03		521.0	217.1	0.208	82	5.06		515.7	44.2	0.028
27	5.03		520.9	228.2	0.230	83	5.09		515.7	50.4	0.025
28	5.04		520.2	349.7	0.367	84	5.10		513.1	61.6	0.024
29	5.06		521.0	454.6	0.528	85	5.06		514.9	97.4	0.066
						86	5.08		514.9	341.3	0.174
30*	6.01	0.102	521.5	147.6	0.193	87	5.10		515.5	447.3	0.240
31	6.05		522.2	152.9	0.181						
32	6.05		521.1	216.0	0.313	88	5.08	0.382	515.5	8.5	0.010
33	6.05		521.2	223.2	0.220	89	5.10		514.3	21.5	0.020
34	6.05		520.5	231.5	0.311	90	5.11		514.1	22.0	0.030
35	6.06		520.5	245.9	0.348	91	5.10		514.1	22.2	0.030
36	6.08		521.3	272.4	0.359	92	5.08		514.3	51.7	0.028
37	6.08		522.6	336.2	0.483	93	5.09		513.8	55.4	0.064
38	6.03		522.1	386.3	0.508						
39	6.07		521.1	535.7	0.569	94	5.06	0.382	533.6	14.8	0.026
40	6.01		521.4	555.5	0.686	95	5.06		533.8	23.9	0.037
41	6.07		520.5	750.2	0.755	96	5.06		533.7	74.2	0.108
						97	5.06		533.6	115.2	0.116
42	6.01	0.161	522.2	73.4	0.097						
43	6.02		522.3	76.0	0.111	98	6.04	0.382	541.2	24.5	0.066
44	6.01		522.7	85.0	0.133	99	6.05		541.0	48.7	0.101
45	6.02		522.7	97.3	0.153	100	6.03		537.2	86.2	0.130
46	6.07		522.2	117.7	0.293	101*	6.06		537.6	89.8	0.134
47	3.09	0.382	499.6	20.7	0.011	102	6.06	0.540	514.0	4.3	0.010
48	3.09		499.4	40.6	0.027	103	6.07		515.3	6.1	0.014
49	3.08		499.6	55.8	0.026	104	6.07		514.9	22.4	0.032
50	3.09		499.7	56.2	0.026	105*	6.10		514.9	26.1	0.036
51	3.09		499.6	60.9	0.032	106	6.06		514.9	36.0	0.042
52	3.10		499.7	61.5	0.029						
53*	3.09		499.1	84.2	0.042	107	6.05	0.540	534.3	5.9	0.010
54	3.10		499.4	126.4	0.061	108	6.04		531.7	22.1	0.013
55	3.09		499.5	126.5	0.054	109	6.06		529.5	25.8	0.031
56	3.10		499.6	133.6	0.066	110	6.06		538.0	93.9	0.052
57	3.08		499.1	161.1	0.072						
58	3.09		499.8	166.1	0.069						

Note: The amount of catalyst was around 1.5. For experiments marked with * the amount of catalyst was around 4 g.

Fig. 3. Typical ζ_{CO} versus τ plots: (a) $P_T = 4.05 \pm 0.04$ MPa, $y_{\text{CO},\text{in}} = 0.102$, $T = 521 \pm 1.5$ K; (b) $P_T = 6.05 \pm 0.05$ MPa, $y_{\text{CO},\text{in}} = 0.102$, $T = 521 \pm 1.5$ K; (c) $P_T = 5.075 \pm 0.025$ MPa, $y_{\text{CO},\text{in}} = 0.382$, $T = 539 \pm 3$ K; (d) $P_T = 5.05 \pm 0.01$ MPa, $y_{\text{CO},\text{in}} = 0.540$, $T = 514 \pm 1.5$ K.

remained unchanged. Within the experimental accuracy no deviations could be observed. We therefore consider the interparticle resistances to be negligibly small.

Accuracy of the results

The maximum absolute error of the chromatographic analysis was 0.3% for each component. The accuracy of the pressure measurements was ± 0.02 MPa and the error in the volumetric flow measurements was negligibly small. The calibrated thermocouples were accurate to better than ± 0.5 K.

The temperature dependence of the reaction rate is non-linear, so inevitably we introduce an error by taking mean catalyst temperatures. Although the temperature differences measured along the bed never exceeded 3 K, it must be borne in mind that the thermocouple sheath and the thermocouple itself by conduction smooth the temperature profile, so the real temperature gradients in the bed are unknown but are definitely higher than the measured ones. We believe the temperature gradients to be the most important cause for the rather high inaccuracies of the experimental results.

Many authors believe that temperatures are controlled better in recycle reactors of the continuous stirred tank type [10, 12, 13, 15], owing to the high gas velocities and therefore good heat transfer conditions. In our opinion, in the laboratory recycle reactors significant errors may also be introduced if the thermo-

couples are not carefully installed. Seyfert and Luft [12] studied the methanol synthesis using a jet-loop reactor at recycle ratios as high as 30 and linear gas velocities of at least 0.12 m s^{-1} . From their data it can be calculated that the temperature difference between the gas and the catalyst particles is at least several degrees. In another recent study of methanol synthesis in a Berty reactor, Villa *et al.* [13] calculated for their system a value of 1.1 K as the maximum temperature difference between the catalyst particle and the surrounding gas. Their calculation is based on an α_p value of $3000 \text{ W m}^{-2} \text{ K}^{-1}$, estimated by them according to Treybal [15]. However, using the very accurate correlations of Martin [16] which are recommended by Westerterp *et al.* [17] for the same conditions, we calculate a value of $1900 \text{ W m}^{-2} \text{ K}^{-1}$ for α_p , which is still a very high value because of the high Reynolds number of around 10 300. For $\alpha_p = 1900 \text{ W m}^{-2} \text{ K}^{-1}$ it is no longer evident that temperature differences can be neglected. It therefore appears to be necessary to measure the catalyst temperature and not the gas temperature because the reaction actually takes place in the catalyst. To this end, the weld of the thermocouple should be installed in the catalyst pellet, using, for example, the technique of Westerterp *et al.* [18].

The apparently high spread in the experimental data shown in Fig. 3 can only be explained partially by the experimental inaccuracies of the flow, temperature, pressure and composition measurements. We believe that there were also additional catalyst promotion effects caused by one or more side products. Klier and co-workers [7] report that even small amounts of water have a strong promoting influence on the copper catalysts. In our system water can be formed in reactions (2), (5) or (6).

Derivation of a reaction rate equation

We examined the 17 reaction rate expressions, which are based on Langmuir-Hinshelwood or Eley-Rideal kinetics, and are listed in Table 3. For the parameter estimation we used the RKPES computer program developed by Klaus and Rippin [19]. This program applies the maximum likelihood approach which for a single-response model reduces to a minimization of the sum of the squares of the residuals according to a Marquardt algorithm. For a plug-flow reactor the conversion is given by

$$\zeta_{\text{CO}} = \int_0^{\tau} R_{\text{CO}} d\tau \quad (12)$$

where R_{CO} is the reaction rate in mol CO converted/kg cat s, and τ is the 'contact time' defined as kg catalyst/mol CO fed per second.

R_{CO} in eqn. (12) is a function of the actual temperature and the fugacities both of the reactants and the product. These fugacities, ϕ_i , divided by the standard-state pressure can be expressed as

$$\phi_i = P_T y_i f_i / P^\circ \quad (13)$$

where P_T is the total pressure, P° the standard-state pressure equal to 0.1 MPa, y_i the mole fraction, and f_i the fugacity coefficient of component i under reaction conditions. At a given feed gas composition, y_i can be expressed as a function of the conversion ζ_{CO} :

$$y_{CO} = \frac{(1 - \zeta_{CO})y_{CO, in}}{1 - 2\zeta_{CO}y_{CO, in}} \quad (14)$$

$$y_{H_2} = \frac{1 - y_{CO, in} - 2\zeta_{CO}y_{CO, in}}{1 - 2\zeta_{CO}y_{CO, in}} \quad (15)$$

and

$$y_M = \frac{y_{CO, in} \zeta_{CO}}{1 - 2\zeta_{CO}y_{CO, in}} \quad (16)$$

For the calculation of the fugacity coefficients f_i , the expressions derived from the Peng–Robinson equation of state [20] can be used:

$$\ln f_i = \frac{b_i}{b} (Z - 1) - \ln(Z - B) - \frac{A}{2B\sqrt{2}} \times \ln \left(\frac{Z + 2.414B}{Z - 0.414B} \right) \left(\frac{2 \sum_j y_j a_{ij}}{a} - \frac{b_i}{b} \right) \quad (17)$$

where

$$A = aP/(RT)^2, \quad B = bP/RT, \quad Z = Pv/RT$$

$$a = \sum_i \sum_j y_i a_{ij}, \quad b = \sum_i y_i b_i, \quad a_{ij} = (1 - \delta_{ij})(a_i a_j)^{1/2}$$

$$a_i(T) = 0.45724 \frac{R^2 T_{ci}^2}{P_{ci}} [1 + K_i(1 - T_{ri})]^2 \quad \text{N m}^4 \text{ mol}^{-2}$$

$$b(T) = b(T_{ci}) = 0.7878 RT_{ci}/P_{ci} \quad \text{m}^3 \text{ mol}^{-1}$$

and

$$K_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$$

Owing to the lack of original data the interaction parameters δ_{ij} are assumed to be equal to zero. Also, for the calculation of the molar volume v we apply the Peng–Robinson equation

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \quad (18)$$

The thermodynamic constants we used to find the fugacity coefficients are specified in Table 5. The applicability of the Peng–Robinson equation of state has been confirmed in other studies [21, 22]. For the thermodynamic equilibrium constant K_{eq} of reaction (1) the following correlation can be derived [23]:

$$\ln K_{eq} = -28.9762 + 11815/T \quad (19)$$

All these data have been put into each of the 17

TABLE 5. Thermodynamic data for CO, H₂ and CH₃OH

Component	CO	H ₂	CH ₃ OH
P_c (MPa)	3.45	1.28	8.078
T_c (K)	134	33.3	512.6
ω	0.049	-0.226	0.564

possible rate equations of Table 3 and, after integration of eqn. (12), experimental τ – ζ_{CO} data sets have been compared with those calculated using the best fit obtained with the RKPES program in which the sum of the squares of the residuals was subjected to a minimization.

In the discrimination between the possible reaction rate equations three criteria were considered:

(1) the value Σ of the sum of the squares of the residuals at the optimum;

(2) the T values, being the ratios of the calculated parameter values to their standard deviations; and

(3) the randomness of the distribution of the residuals.

Three expressions, corresponding to the rate expressions 1, 4 and 12 in Table 3, appeared to give the best fit to our experimental results. The parameter values, the corresponding T values, and the Σ values are given in Table 6.

Rate equations 1 and 4 give objective function values Σ of 0.210 and 0.132, respectively, while the simple expression 12 results in a less accurate fit with $\Sigma = 0.625$. On the other hand, the parameters found for rate equation 12 have the highest T values. The T values apparently increase with decreasing number of model parameters. Moreover, the standard deviations of the activation energies are higher than those of the corresponding frequency factors; this issues from the uncertainties in the temperature readings, as has been discussed above.

It can be seen in Fig. 4 that the distribution of the residuals around the zero axis for all three rate expressions in Table 6 is symmetrical over the whole response domain. Other rate expressions in Table 3 failed because of either much higher Σ values or asymmetrical distributions of the residuals. As an example of the latter, the residuals for rate expression 5 are plotted in Fig. 5.

Rate expression 1 has also been found by other authors. Villa *et al.* [13] proposed expression 1 and claimed that the methanol adsorption term is negligible; this is in complete agreement with our findings. In view of the low T values in our parameter estimation, we are unable to draw conclusions on the most probable reaction mechanism or rate expression.

For our catalyst we may use the following chemical rate equations:

$$R_{CO} = \frac{2.68 \times 10^9 \exp(-18400/T)(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})}{(1 + 0.069\phi_{CO} + 6.19 \times 10^{-8} \exp(6610/T)\phi_{H_2})^3} \quad (20)$$

or

$$R_{CO} = \frac{18.01 \exp(-9032/T)(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})}{(1 + 2.97 \times 10^{-4} \exp(3539/T)\phi_{CO} + 2.59 \times 10^{-4} \phi_{CO}\phi_{H_2}^2)} \quad (21)$$

with R_{CO} in mol CO/kg cat s.

In order to compare the results of Seyfert and Luft [12] with our results, we extrapolated their correlation

TABLE 6. Rate expressions obtained

Correlation No. for R_M in Table 3	Parameter ^a	Value	T value defined in text	Σ
1: $\frac{k(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})}{(1 + A\phi_{CO} + B\phi_{H_2} + C\phi_M)^3}$	k_0	2.68×10^9	3.07	0.21
	E_k/R	18 400	2.67	
	A_0	0.069	5.9	
	E_A/R	0	—	
	B_0	6.19×10^{-8}	4.53	
	E_B/R	-6610	0.48	
	C_0	0	—	
4: $\frac{k(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})}{1 + A\phi_{CO} + B\phi_{CO}\phi_{H_2}^2}$	k_0	18.01	4.38	0.132
	E_k/R	9032	1.22	
	A_0	2.97×10^{-4}	2.4	
	E_A/R	-3539	0.225	
	B_0	2.59×10^{-4}	3.85	
	E_B/R	0	—	
12: $k(\phi_{CO}\phi_{H_2}^2 - \phi_M/K_{eq})/\phi_{H_2}$	k_0	1.51×10^{-3}	20.2	0.625
	E_k/R	3019	1.46	

^a k_0 in mol CO converted/kg cat s; A , B , C and D are dimensionless; E_i/R in K.

Fig. 4. Residuals as a function of the calculated conversions: (a) for expression 1, (b) for expression 4, (c) for expression 12.

Fig. 5. The residual conversion response obtained for rate expression 5 in Table 3.

to our experimental range. At 513 K and 6 MPa and with $y_{\text{CO}, \text{in}} = 0.33$ and $y_{\text{H}_2, \text{in}} = 0.67$ the initial reaction rates are 8.36×10^{-3} , 6.25×10^{-4} , and 8.85×10^{-4} mol/kg cat s for the correlation of Seyfert and Luft and for our expressions 1 and 4, respectively. At $\zeta_{\text{CO}} = 0.20$ we calculated values of 6.86×10^{-3} , 5.5×10^{-4} , and 7.8×10^{-4} mol/kg cat s, respectively.

Discussion and conclusions

Using the RKPES computer program for a statistical optimization of the non-linear model parameters, three rate expressions fit the experimental data equally well. The standard deviations of the parameter values found are high.

The BASF type S3-85 Cu/ZuO/Al₂O₃ catalyst also catalyses the methanol synthesis well with a feed gas free of CO₂. At low partial pressures of CO the catalyst remains active for many months. On the other hand, at high partial pressures of CO, for example above 5 MPa, a rapid and irreversible degradation of the catalyst is observed. Dimethyl ether, formed by decomposing methanol, also deactivates the catalyst irreversibly at high partial pressures.

In the absence of CO₂, we measured reaction rates which were 5–15 times lower than those found by other authors for synthesis gases containing several per cent of CO₂. The catalyst selectivity remained high. In the course of the study several independent samples of the catalyst were used, so any accidental influence of the sample properties is out of the question.

The side reactions and the rather high uncertainties about the true catalyst temperatures together lead to rather inaccurate results for rate expressions obtained in a laboratory reactor of the integral tubular type. We do not believe that it is possible to obtain better accuracy in an integral reactor. We expect bet-

ter results in a gradientless laboratory reactor. We have started such experiments and will report on them in due course.

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Nomenclature

A_0, B_0, C_0, D_0	frequency factors
E	activation energy, J mol ⁻¹
f	fugacity coefficient
k	rate constant, mol CO converted/kg cat s
K_{eq}	equilibrium constant
m_{cat}	mass of catalyst, kg
P_T	total pressure, Pa
R_{CO}	reaction rate, mol CO converted/kg cat s
R	gas constant = 8.3144 J mol ⁻¹ K ⁻¹
T	temperature, K
v	molar volume, mol m ⁻³
y	mole fraction
Z	compressibility factor
α_p	particle heat transfer coefficient, W m ⁻² K ⁻¹
ζ_{CO}	CO conversion
τ	'contact time', kg cat s/mol CO fed
ϕ	fugacity divided by standard state pressure
Φ	molar flow, mol s ⁻¹
ω	Pitzer's acentric factor

Subscripts

c	critical parameter
i	component i
in	inlet
out	outlet
p	particle
r	reduced parameter

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