

Steam reforming of methanol over a Cu/ZnO/Al₂O₃ catalyst: a kinetic analysis and strategies for suppression of CO formation

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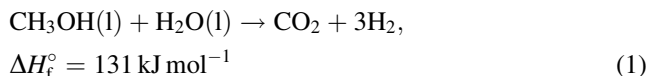
Abstract

Steam reforming of methanol ($\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$) was studied over a commercial Cu/ZnO/Al₂O₃ catalyst for production of hydrogen onboard proton exchange membrane (PEM) fuel cell vehicles. A simple power-law rate expression was fitted to experimental data in order to predict the rates of CO₂ and H₂ formation under various reaction conditions. The apparent activation energy (E_a) was estimated to be 100.9 kJ mol⁻¹, in good agreement with values reported in the literature. Appreciable amounts of CO by-product were formed in the reforming process at low contact times and high methanol conversions. Being a catalyst poison that deactivates the electrocatalyst at the fuel cell anode at concentrations exceeding a few ppm, special attention was paid to the pathways for CO formation and strategies for its suppression. It was found that increasing the steam–methanol ratio effectively decreases CO formation. Likewise, addition of oxygen or air to the steam–methanol mixture minimises the production of CO. By shortening the contact time and lowering the maximum temperature in the reactor, CO production can be further decreased by suppressing the reverse water–gas shift reaction. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen production; Methanol; Steam reforming; Cu/ZnO/Al₂O₃ catalyst; Carbon monoxide; PEM fuel cell vehicles

1. Introduction

Extensive research efforts are focused on the development of proton exchange membrane (PEM) fuel cells for vehicle propulsion and small scale power generation. Although hydrogen is the preferred fuel, PEM fuel cell vehicles will probably use liquid fuels at least in the early stages of commercialisation due to problems associated with safety and handling of hydrogen. Methanol has been identified as a highly suitable liquid fuel, offering a high hydrogen–carbon ratio, an absence of carbon–carbon bonds and a potentially high production capacity. A hydrogen-rich gas can be produced onboard the vehicle by steam reforming of methanol (SRM) over a copper-based catalyst [1–15]:



Unfortunately, the SRM process produces CO as by-product in appreciable amounts. The precious metal electrocatalyst at the fuel cell anode is poisoned by CO in concentrations exceeding a few ppm. Hence, present-day reforming technologies require some type of a CO clean-up step prior to the

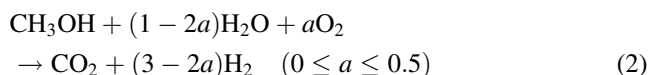
fuel cell, such as selective CO oxidation or methanation, or a palladium membrane. Keeping this in mind, reduction of the CO-level already in the reforming reactor appears to be an attractive option, minimising the size and energy requirements of the fuel processor system. There are various strategies for CO abatement during SRM, either by catalytic or reaction engineering solutions.

One of the objectives of the present study is to gain increased understanding of the mechanisms for CO formation during methanol reforming and how it can be avoided. We first report on a kinetic study of the SRM process over a commercial Cu/ZnO/Al₂O₃ catalyst from Süd-Chemie (G-66 MR). A simple power-law rate expression, previously developed by Jiang et al. [7,8] by using an empirical approach, is fitted to the experimental data. Subsequently, reaction parameters such as steam–methanol ratio, contact time, reaction temperature and oxygen addition and their influence on CO formation are discussed.

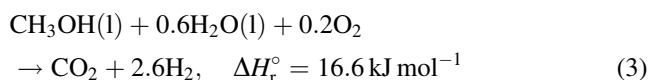
Addition of oxygen to the SRM process is common practice for the industrial production of syn gas from natural gas [16,17]. The reaction with steam is highly endothermic and consumes large amounts of energy. Hence, by addition of oxygen or air, reforming can be carried out close to thermal neutrality or under slightly exothermic conditions by utilising heat from the exothermic oxidation reaction. In

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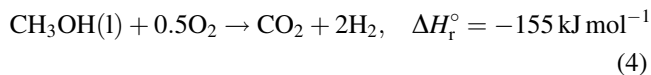
other words, the process can be made thermally self-sustaining with no need for external heat exchange. More recently, feeding a mixture of air, steam and methanol over a copper-based catalyst has been studied for the production of hydrogen for fuel cell vehicles under close-to-adiabatic conditions with extremely low CO-levels [18–25]. The process, so-called combined reforming of methanol (CRM), is sometimes referred to as autothermal reforming when operated close to thermal neutral conditions. In its general form, the equation for CRM can be written as:



For the CRM experiments in this study, feed compositions proposed by Velu et al. [24] were used. These authors found that molar ratios of $\text{H}_2\text{O}/\text{CH}_3\text{OH} = 1.3\text{--}1.6$ and $\text{O}_2/\text{CH}_3\text{OH} = 0.2\text{--}0.3$ resulted in the optimum performance in the combined process, termed oxidative steam reforming in their work. Using ratios of 1.3 and 0.2, respectively, the general form of Eq. (2) translates to Eq. (3) below, based on the assumption that all oxygen is consumed while steam is in excess. This assumption is reasonable considering the fast and highly exothermic nature of the oxidation reaction.



The constant a in Eq. (2) equals 0 for pure SRM and 0.5 for pure partial oxidation of methanol (POM), the equation of which is given below:



Recently, the POM reaction over copper-based catalysts has attracted attention as an alternative to the SRM route for hydrogen production in fuel cell vehicles [26–28]. In this study, however, mainly results obtained from SRM and CRM are reported and discussed.

2. Experimental

A commercial Cu/ZnO/Al₂O₃ catalyst from Süd-Chemie (G-66 MR) was used in all experiments. Data on catalyst properties provided by the manufacturer are given in Table 1.

Catalytic activity measurements were carried out at atmospheric pressure in a tubular quartz reactor (6 mm i.d.). The reactor was placed inside a programmable furnace and a type K thermocouple located in a pocket in the centre of the catalyst bed was used to measure the reaction temperature. Pure methanol or premixed water–methanol was fed to a custom-built vaporiser by means of a Braun Perfusor F syringe pump. The carrier gas, containing oxygen for the POM and CRM experiments, was also introduced into the vaporiser. The air flow was adjusted by a Brooks 5850TR

Table 1

Typical physical properties of the Süd-Chemie G-66 MR methanol reforming catalyst, as reported by the manufacturer

Chemical composition (nominal)	
CuO	66 wt.%
ZnO	23 wt.%
Al ₂ O ₃	11 wt.%
Pellet size	6 mm × 3.5 mm
Side crush strength	170 N (average); max. 5% <80 N
Bulk density	1.1 kg dm ⁻³
Specific surface area	70 m ² g ⁻¹

mass flow controller. All tubing was heated to avoid condensation in the system.

The composition of the feed and product gases was determined by on-line gas chromatography (GC), using a Varian GC3800 equipped with a thermal conductivity detector (TCD). Helium was used as the carrier gas, providing acceptable sensitivity for the carbon oxides. The components were separated by HayeSep T (“air”, CO₂, H₂O, CH₃OH) and MolSieve 13X (H₂, O₂, N₂, CO) columns connected in a series/by-pass configuration. In the following discussion, the ratio CO/(CO + CO₂) will be referred to as the CO-selectivity.

The catalyst was crushed, sieved and diluted with silica prior to loading the reactor. By doing this, the pressure drop over the catalyst bed could be minimised, gas flows and mass transport conditions were reproducible, and the formation of hot-spots could be avoided. Reduction was performed by exposing the catalyst to 10% H₂/N₂ flowing at 100 ml min⁻¹ and increasing the temperature to 300 °C at 10 °C min⁻¹. This temperature was maintained for 1 h. Subsequently, the temperature of the furnace was lowered to around 150 °C before switching from the H₂–N₂ mixture to the methanol-containing feed. Fresh catalysts were used in all experiments to avoid ageing effects.

The values of W/F were chosen experimentally to enable adequate measurements of product composition and to avoid thermal runaway during the exothermic POM reaction. No efforts were made in order to optimise this value with respect to catalyst performance. The experimental conditions are listed in Table 2.

Table 2

Standard experimental conditions for catalytic activity measurements (flow rates given at 20 °C and 1 atm)

Catalyst load	50 mg (diluted to 500 mg with silica)
Particle size	0.12–0.25 mm
Temperature	175–350 °C
Pressure	1.0 atm
Molar H ₂ O/CH ₃ OH ratio	1.3 (SRM and CRM)
Molar O ₂ /CH ₃ OH ratio	0.2 (POM and CRM)
CH ₃ OH (l) feed rate	1.3 ml h ⁻¹ (Baker, >99.8%)
H ₂ O (l) feed rate	0.7 ml h ⁻¹ (SRM and CRM)
Air flow rate	14 ml min ⁻¹ (POM and CRM)
Total flow rate	~230 ml min ⁻¹
N ₂ flow rate	Balance (190–210 ml min ⁻¹)

3. Results

Fig. 1 shows a typical series of experimental results for SRM over the Cu/ZnO/Al₂O₃ catalyst from Süd-Chemie. Methanol conversion follows a typical S-shaped curve and reaches 100% at about 320 °C. The product gas composition indicates that H₂ and CO₂ are produced at an approximate 3:1 ratio, as expected, with CO formation initiating at higher temperatures when methanol approaches complete conversion. The H₂ content in the product approaches the maximum attainable value of 70% at ~320 °C. The theoretical maximum H₂ concentration in the product gas for the SRM reaction is 75%, but due to the excess of steam, the practically attainable value is lower.

3.1. The kinetic model

First, a kinetic analysis of the SRM reaction was undertaken. The model is based on a simple empirical rate law expression derived by Jiang et al. [7,8] for a Cu/ZnO/Al₂O₃ catalyst from BASF (S3-85), sold commercially for methanol synthesis. The catalyst used in their study consisted of 31.7% CuO, 49.5% ZnO and 18.8% Al₂O₃ and possessed a BET surface area of 83 m² g⁻¹. For comparison, the physical data of the Süd-Chemie catalyst used in this study are summarised in Table 1.

The rate equation proposed by Jiang et al. [7,8] is divided into two parts, depending on the H₂ partial pressure:

$$r_{\text{SRM}} = k P_{\text{CH}_3\text{OH}}^{0.26} P_{\text{H}_2\text{O}}^{0.03} \quad (P_{\text{H}_2} < 7 \text{ kPa}) \quad (5)$$

$$r_{\text{SRM}} = k P_{\text{CH}_3\text{OH}}^{0.26} P_{\text{H}_2\text{O}}^{0.03} P_{\text{H}_2}^{-0.2} \quad (P_{\text{H}_2} > 7 \text{ kPa}) \quad (6)$$

Using these expressions, a kinetic model was fitted to the experimental results obtained in this study under various reaction temperatures and methanol feed rates.

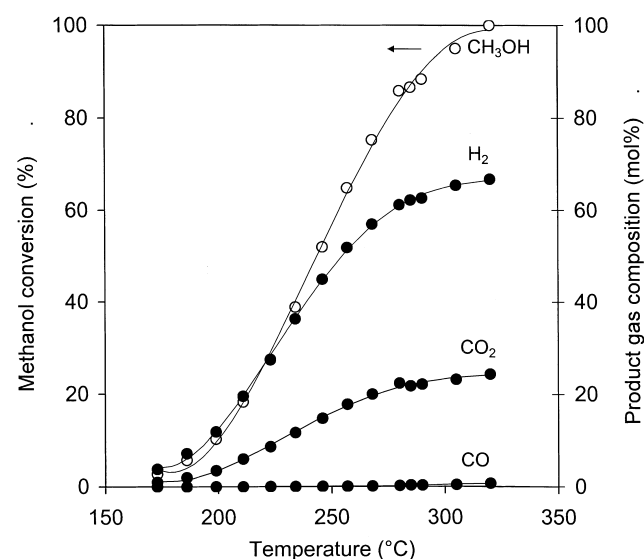


Fig. 1. The temperature dependence of methanol conversion and product composition during methanol steam reforming over the G-66 MR Cu/ZnO/Al₂O₃ catalyst from Süd-Chemie (H₂O/CH₃OH = 1.3).

For a tubular packed bed reactor (PBR), the design equation was taken to be [29]:

$$F_{\text{CH}_3\text{OH},0} dX = -r_{\text{SRM}} dW \quad (7)$$

Internal mass transfer resistance was considered negligible and isothermal reaction conditions were assumed inside the porous bed. The pressure drop was accounted for though found to be negligible (~10³ Pa). A function describing the reaction rate constant $k(T)$ in Eqs. (5) and (6) and its variation with temperature was first determined. For this purpose, activity measurements at four different methanol–water feed rates (0.5–3.0 ml h⁻¹) were carried out at temperatures between 175 and 350 °C. The methanol conversion was used as a criterion for comparison of experimental data with simulated, which enabled an adequate determination of $k(T)$. As demonstrated in Fig. 2, the rate constant behaves according to an Arrhenius-type expression at temperatures below ~493 K, whereas at higher temperatures, mass transfer starts to limit the reaction kinetics. Hence, an Arrhenius exponential function was fitted to the experimentally obtained values of $k(T)$ only in the region between 448 and 493 K (175–220 °C). The equation is given below:

$$k(T) = 1.9 \times 10^{12} \exp\left(\frac{-100.9 \text{ kJ mol}^{-1}}{RT}\right) \quad (8)$$

The calculated apparent activation energy (E_a) of 100.9 kJ mol⁻¹ agrees well with values of 77–105 kJ mol⁻¹ reported in the literature (see Table 3). Subsequently, the experimental results were used as a basis to fit a fifth degree polynomial describing the rate constant's variation in the entire temperature regime. This function was then inserted into Eqs. (5) and (6), using the kinetics for a PBR. Fig. 3a and b demonstrate how the obtained model is able to predict

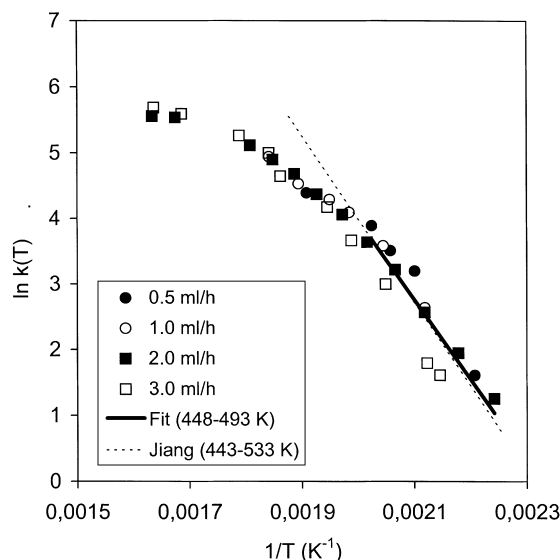
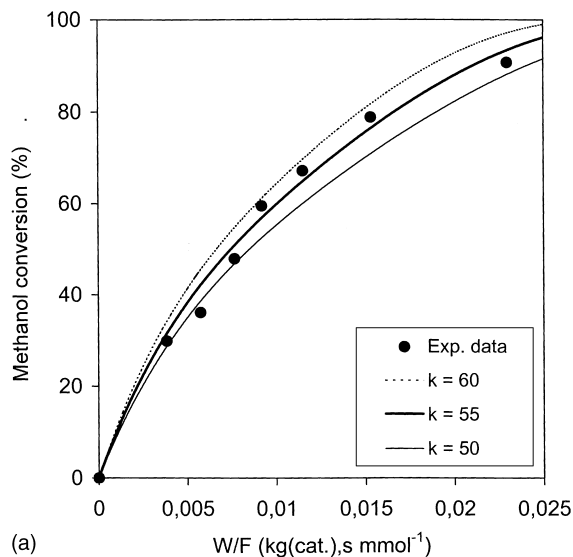


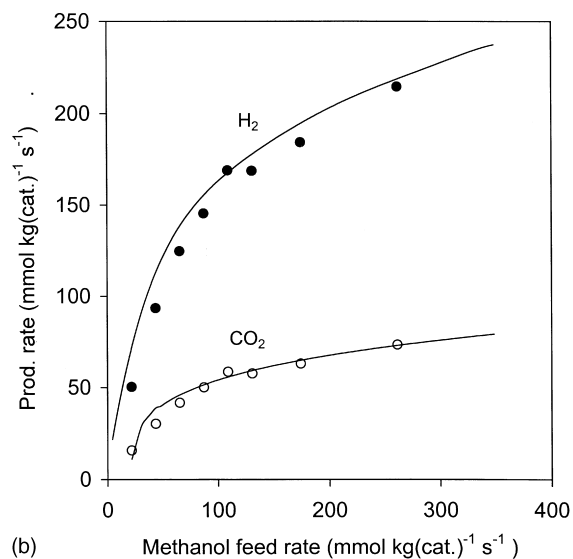
Fig. 2. Arrhenius plot for four different methanol–water feed rates at temperatures between 448 and 623 K. The solid line represents the linear fit in the kinetically controlled region. The dotted line represents the results by Jiang et al. [7].

Table 3
Apparent activation energies (E_a) for the steam reforming reaction over Cu/ZnO/Al₂O₃ catalysts as estimated by kinetic experiments

E_a (kJ mol ⁻¹)	Temperature range (°C)	Reference
100.9	175–220	Agrell et al. (present study)
83 (±3.5%)	230–280	[22]
102.8	160–260	[12]
105.1	170–260	[7]
77	160–200	[5]



(a)



(b)

Fig. 3. (a) Methanol conversion plotted vs. contact time for steam reforming at 220 °C and H₂O/CH₃OH = 1.3. Experimental data and predicted conversions at $k(T) = 50, 55$ and $60 \text{ mmol kg}^{-1} \text{ s}^{-1} \text{ kPa}^{-0.29}$. (b) The predicted and observed production rates of H₂ and CO₂ plotted vs. the feed rate of methanol during steam reforming at 220 °C and H₂O/CH₃OH = 1.3 ($k(T) = 55 \text{ kg}_{\text{cat}}^{-1} \text{ s}^{-1} \text{ kPa}^{-0.29}$).

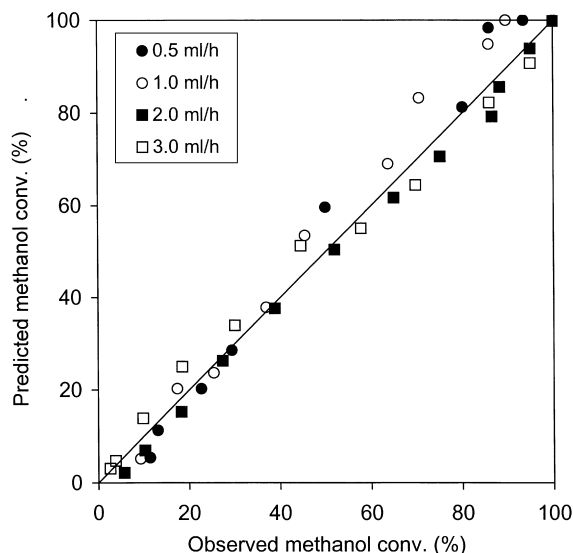


Fig. 4. Parity plot showing the predicted vs. the observed methanol conversion during steam reforming in the 175–350 °C temperature range at four different methanol–water feed rates (H₂O/CH₃OH = 1.3).

methanol conversion and the production rates of H₂ and CO₂ quite accurately at various liquid feed rates when maintaining the reaction temperature at 220 °C.

Fig. 4 shows a parity plot for all four investigated feed rates in the 175–350 °C temperature interval. For the lower feed rates (0.5 and 1.0 ml h⁻¹), some experimental difficulties were encountered due to variations in the composition of the inlet stream. Instabilities occurred when attempting to generate such low liquid flow rates. The GC measurements of methanol conversion displayed variations of up to 8% and hence, an accurate determination of the outlet stream composition could not be obtained. As seen in Fig. 4, the correlation between experimental results and simulated data was less accurate at these lower feed rates.

The inhibiting effect of H₂ on the reaction at partial pressures exceeding 7 kPa was taken into account in the model. Depending on the concentration of H₂ in the reactor, the appropriate equation was used. As shown in Fig. 5, the proposed inhibition agrees rather well with the experimental results.

3.2. Process parameters and CO formation

After establishing the validity of the rate expression, further work concentrated on varying the reaction conditions and studying the influence of these parameters on reaction rate and product distribution. Fig. 6 shows the influence of H₂O/CH₃OH ratio on CO formation in the SRM reaction. As shown, the CO-selectivity at 320 °C increases from less than 3 to ~11% when the molar H₂O/CH₃OH ratio is changed from 1.3 to 1.0. Clearly, steam in excess of the amount required by stoichiometry effectively suppresses CO formation.

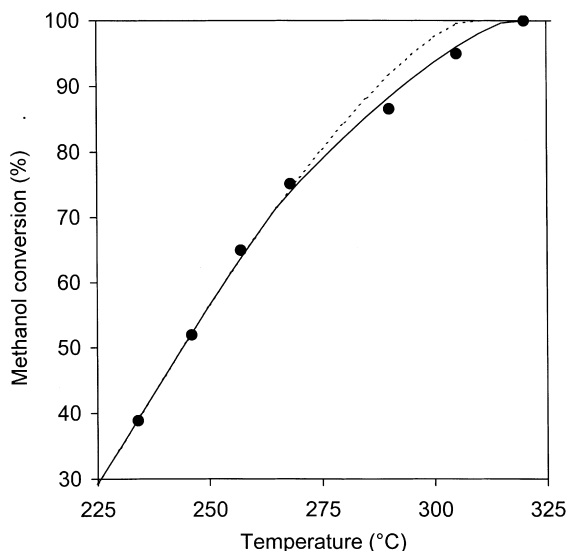


Fig. 5. Methanol steam reforming over Cu/ZnO/Al₂O₃ (H₂O/CH₃OH = 1.3) taking H₂ inhibition at partial pressures above 7 kPa into account (solid line) and without any correction (dotted line).

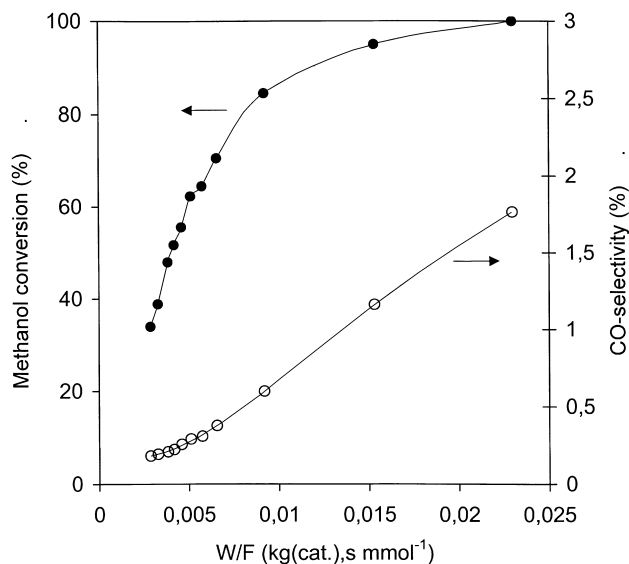


Fig. 7. Methanol conversion and CO-selectivity plotted vs. pseudo-contact time during methanol steam reforming at 260 °C over Cu/ZnO/Al₂O₃ (H₂O/CH₃OH = 1.3).

Another series of experiments was carried out by varying the pseudo contact time, i.e. changing the methanol–water feed rate while keeping the total flow rate into the reactor constant. The effect on methanol conversion and CO-selectivity at 260 °C is clearly demonstrated in Fig. 7. At longer contact times, higher conversions are attained, as expected. Likewise, the CO-levels increase almost linearly with increasing contact time.

Addition of oxygen to the SRM reaction was also investigated (CRM), as well as the reaction between oxygen and methanol in absence of steam (POM). The variations in methanol conversion with reaction temperature for all three

processes are shown in Fig. 8. During CRM, with oxygen present in the feed mixture, there is clearly an inhibiting effect on methanol conversion at temperatures up to about 250 °C compared to SRM. At higher temperatures, the methanol conversion follows a similar trend in both processes. The level of CO in the product gas is also affected by the addition of oxygen. As shown in Fig. 9, the CO-selectivity is lower at temperatures exceeding 260 °C when oxygen is added. The selectivity to CO is reduced to about half at 320 °C, from 3 to ~1.5%, by adding oxygen to the reaction mixture. When studying the POM process (Fig. 8), it can be observed that methanol conversion follows a trend

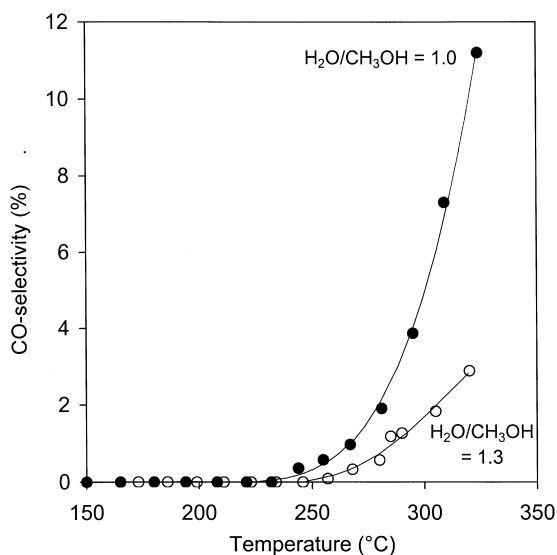


Fig. 6. The effect of molar steam–methanol ratio on CO-selectivity during SRM over Cu/ZnO/Al₂O₃ at a liquid feed rate of 2.0 ml h⁻¹.

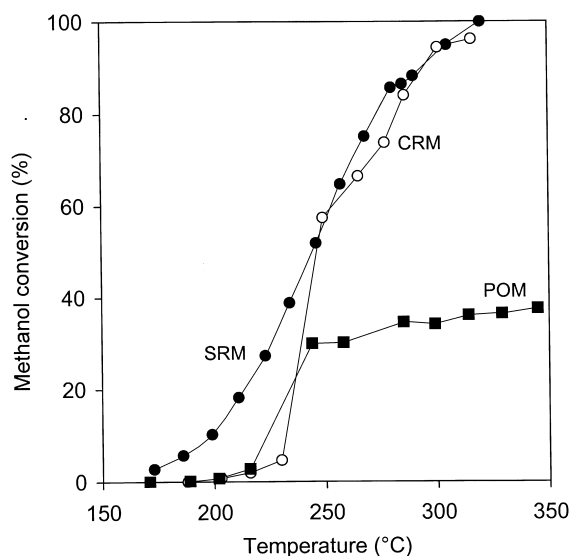


Fig. 8. The effect of reaction temperature on methanol conversion for steam reforming (SRM), combined reforming (CRM) and partial oxidation of methanol (POM) (H₂O/CH₃OH = 1.3; O₂/CH₃OH = 0.2).

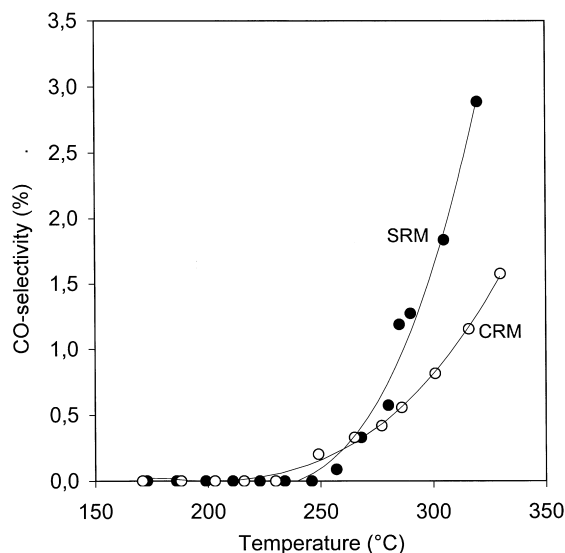


Fig. 9. The effect on CO-selectivity of oxygen addition ($O_2/CH_3OH = 0.2$) during methanol steam reforming at $H_2O/CH_3OH = 1.3$.

quite similar to that during CRM up to 210 °C, i.e. slowly increasing in the 190–210 °C temperature range and then sharply increasing to an almost constant value at 240 °C.

Fig. 10 shows the ΔT between the catalyst bed and the furnace wall plotted against the reaction temperature for all three processes. For the endothermic SRM reaction there is a monotonic decrease in ΔT at differential methanol conversions. As shown in Fig. 1, CO formation is initiated when approaching complete conversion of methanol around 300 °C, where the slope of the ΔT -curve levels off. The POM reaction is highly exothermic, hence the steep increase in reaction heat, accelerating from 215 °C and reaching a maximum value at 260 °C. The maximum occurs at a

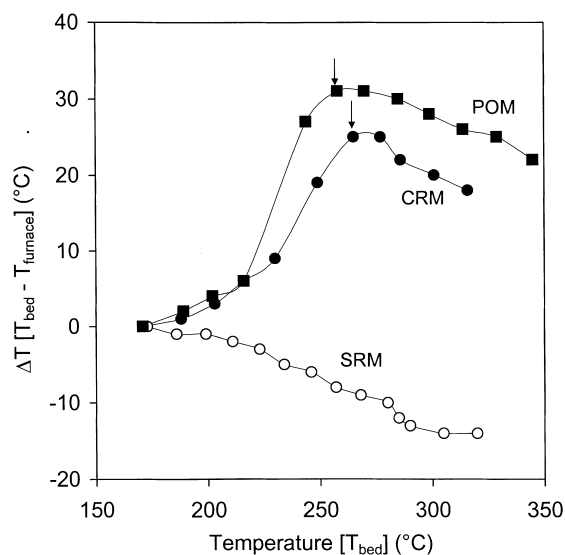
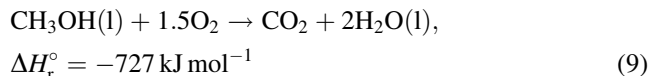


Fig. 10. The ΔT between the catalyst bed and the furnace wall plotted against the reaction temperature for steam reforming (SRM), combined reforming (CRM) and partial oxidation of methanol (POM). The arrows indicate the temperatures at which all oxygen has been converted.

methanol conversion of about 30% and corresponds to the point where all oxygen is consumed. This is evidence of oxygen being at least partially consumed by complete combustion of methanol (Eq. (9)), followed by SRM using the water that has been produced. During SRM, the heat of reaction decreases, hence the subsequent negative slope of the ΔT -curve.



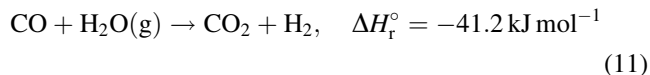
As expected, the profile for CRM is similar to POM but it does not reach as high values, being a combination of POM and SRM. Again, the maximum of the ΔT -curve corresponds to complete conversion of oxygen, hence evidencing a sequential process, i.e. methanol combustion followed by SRM. The vertical arrows in Fig. 10 indicate the temperatures at which all oxygen has been converted.

4. Discussion

4.1. Reaction pathway

There has been some debate in the literature concerning the pathway for production of CO_2 and H_2 by SRM. Much attention has been focused on the mechanism for CO by-product formation and at least three different reaction schemes have been suggested.

The decomposition-WGS sequence has been proposed by some authors [1,2,5,6]. In this scheme, CO is believed to be a primary product, subsequently converted into CO_2 in the WGS reaction, accompanied by H_2 formation:



For instance, Santacesaria and Carrà [5] studied the SRM kinetics over a commercial low-temperature $Cu/ZnO/Al_2O_3$ shift catalyst from BASF in a continuous stirred-tank reactor (CSTR). Negligible amounts of CO were found in the product, which was thought to be in agreement with the attainment of WGS equilibrium after methanol decomposition. The decomposition-WGS sequence was suggested and the decomposition step was found to be rate-limiting.

Other researchers report on a direct mechanism for the SRM process, where CO_2 and H_2 are formed from methanol in a single step [11–13,22]. For instance, Geissler et al. [22] studied commercial $Cu/ZnO/Al_2O_3$ catalysts and from measurements showing lower CO concentrations than determined by equilibrium calculations they concluded that the SRM reaction is a single-step process, i.e. not a consecutive reaction consisting of methanol decomposition followed by WGS.

According to the discussion above, the WGS reaction clearly plays an important role in the SRM process, either by

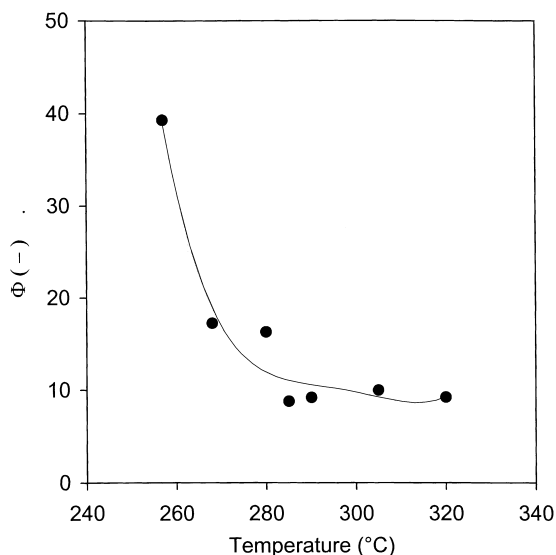


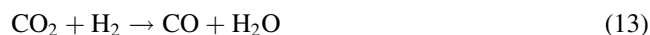
Fig. 11. The ratio Φ given by Eq. (12) plotted against reaction temperature in the region where CO was observed experimentally. SRM at a liquid feed rate of 2.0 ml h^{-1} and $\text{H}_2\text{O}/\text{CH}_3\text{OH} = 1.3$ (see Table 2 for reaction conditions).

converting the CO into CO_2 in the decomposition-WGS scheme, or by adjusting the CO/CO_2 ratio in the direct single-step SRM sequence. In general, CO-levels far below those predicted by equilibrium calculations are observed, also in the present study.

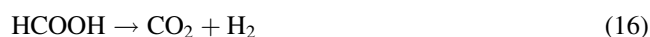
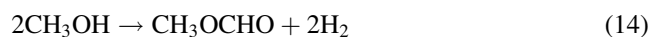
The equilibrium of the WGS reaction is strongly influenced by temperature, lower temperatures favouring CO_2 and H_2 formation [30]. In Fig. 11, the ratio Φ given by Eq. (12) has been plotted against the reaction temperature in the region where CO formation was observed experimentally in the SRM reaction at a liquid feed rate of 2.0 ml h^{-1} and $\text{H}_2\text{O}/\text{CH}_3\text{OH} = 1.3$ (see Table 2 for reaction conditions):

$$\Phi = \frac{1}{K_{\text{eq}}} \frac{P_{\text{H}_2} P_{\text{CO}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}} \quad (12)$$

The product gas is clearly far from equilibrated, CO-levels being well below those predicted by equilibrium. This result supports a reaction scheme in which CO is produced by the reverse water–gas shift (RWGS) reaction:



A methyl formate reaction route, in which no CO takes part, has been suggested by other researchers [4,7–9]. No WGS is involved in this reaction scheme, which is thought to proceed via dehydrogenation to methyl formate. Methyl formate then hydrolyses to formic acid, which decomposes into CO_2 and H_2 , which are the primary products of the reaction:



The kinetic study by Jiang et al. [7,8] using $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst from BASF (S3-85) suggested that methanol dehydrogenation controls the rate of SRM. These authors argued that the decomposition-WGS scheme can be ruled out considering that the concentration of CO in the product is well below that predicted by equilibrium calculations. The CO observed was suggested to be a primary product, produced by decomposition of methyl formate:



Peppley et al. [11] studied the reaction network for SRM over a $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst from BASF (K3-110). They support neither a reaction scheme where methanol decomposition is followed by WGS, nor the direct reaction between methanol and steam followed by RWGS. Instead, they claim that all three reactions (SRM, WGS and decomposition) must be included in the model to fully understand the reaction network, indicating that SRM may be a single-step process. These authors developed a comprehensive kinetic model including surface mechanisms. The model suggested that two distinct types of catalyst sites are required for the production of H_2 by reaction between methanol and steam, one for the SRM and WGS reactions and another for the methanol decomposition reaction.

It appears to be a general observation that CO is formed at high methanol conversions and long contact times. For instance, Breen and co-workers [9,10] investigated ZrO_2 -containing $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalysts and found that the conversion of methanol was complete at temperatures exceeding 345°C . CO started to form above 300°C , even though its formation was thermodynamically permitted at much lower temperatures. Additional experiments indicated that CO was not formed at all at low contact times. Its concentration only became significant when methanol was almost completely consumed at higher temperatures. The results indicated that CO is a secondary product, formed at higher temperatures by the RWGS reaction. This is in full agreement with results from the present study. We found that the level of CO decreases with decreasing contact time, suggesting that a short residence time in the catalyst bed effectively hinders CO production by RWGS. In addition, the forward WGS reaction, consuming CO, is favoured by lower temperatures. However, the mechanism for formation of the CO by-product remains a controversial topic. It should be noted that only some researchers observe methyl formate and formic acid intermediates during SRM. In the present study, neither of these compounds were analysed in the reaction product.

4.2. Consequences for catalyst and reactor design

The discussion in the previous section has consequences for choosing the optimal catalyst and operating conditions for a methanol reformer. It is possible to operate the catalyst under conditions where CO concentrations are much lower than those predicted by thermodynamics, as long as the

temperature is low enough and the contact time short enough to prevent complete conversion of methanol. Under these conditions, the contribution from the RWGS reaction is insignificant. In other words, there is a trade-off between high methanol utilisation and low CO-levels. At this stage it should be pointed out that the fuel cell may be negatively affected by unconverted methanol in the reformat.

The addition of oxygen to the SRM reaction appears to be an effective way of decreasing the CO content in the product. Integrally, the CRM process can be considered a combination of SRM and POM, hence converting methanol under close to adiabatic reaction conditions. However, by studying the process differentially, it is clear that these two reactions occur consecutively. Oxygen is first converted via combustion of methanol (Eq. (9)), followed by reaction between the remaining methanol and the water produced. In a tubular PBR system, which will have concentration and temperature gradients along the length of the catalyst bed, this provides challenging opportunities for new and innovative reactor design. Heat produced in the upstream combustion zone, near the entrance of the reactor, needs to be transported to the downstream zone, near the reactor exit where the endothermic SRM reaction occurs. For instance, if a tubular PBR with a high degree of back-mixing is used, resembling a CSTR, the reaction heat produced upstream can be utilised effectively for the endothermic reforming reaction downstream. However, this type of reactor is hardly feasible in a vehicular application.

De Wild and Verhaak [14] have described a methanol steam reformer using a highly integrated approach to heat transfer. By using a heat-exchanger type reactor, consisting of corrugated aluminium plates coated with catalyst, SRM and combustion of H₂-rich anode off-gases and/or fuel methanol can be carried out in parallel channels, thus providing excellent heat transfer characteristics. Two types of catalysts were used in this system, i.e. a copper-based reforming catalyst and an efficient combustion catalyst, which does not deactivate at high temperatures.

A similar approach could be the one of choice for the combined CRM system. A catalyst other than the traditional copper-based one, or perhaps a combination of materials, may be better suited for the CRM system. In the upstream combustion zone, where high temperatures and hot spots may occur, copper catalysts risk deactivation by sintering. Copper has a low Hüttig temperature [31], reflected by its relatively low melting point (1083 °C), and it is well-known that Cu/ZnO/Al₂O₃ catalysts suffer thermal deactivation at temperatures exceeding 300–350 °C [30,32]. Therefore, a staged catalyst system with an efficient methanol combustion catalyst in the upstream region and a copper-based reforming catalyst downstream could be the solution of choice, thus reducing the risk of catalyst failure by deactivation.

During CRM and POM, it was observed that there is an upward shift in the temperature at which the catalyst starts producing H₂, when compared to pure SRM. It appears as if the presence of oxygen deactivates the catalyst surface at

low methanol conversions. One explanation for this observation could be that the surface copper is oxidised to copper oxide, thus rendering the catalyst inactive for H₂ production. At higher methanol conversions when all oxygen has been consumed by combustion, the gas mixture is again reductive and copper is transformed into its metallic form. Therefore, in a practical application, care must be taken not to expose the catalyst to air in order to avoid deactivation by oxidation.

If oxygen is completely converted by combustion of methanol (Eq. (9)) in a first step during CRM, this will lead to a decreased level of methanol and an increased water content in the reaction mixture. At initial molar ratios of O₂/CH₃OH = 0.2 and H₂O/CH₃OH = 1.3, the corresponding H₂O/CH₃OH ratio after complete consumption of oxygen will be 1.8 (molar). In other words, CRM is merely a way of increasing the H₂O/CH₃OH ratio, hence suppressing CO formation by hindering the RWGS reaction.

The preferred choice of process, i.e. CRM or pure SRM with a high H₂O/CH₃OH ratio, depends on reactor type and application. If the heat produced by methanol combustion with oxygen can be fully utilised, CRM may be the preferred option. In a pressurised system where the oxidant (air) needs to be provided at an elevated pressure, the energy required for compression constitutes a substantial disadvantage, clearly favouring pure SRM. In automotive PEM fuel cell applications, a slight overpressure is generally desired in the fuel cell. Furthermore, a high H₂ content in the reformat promotes the anode reaction in the fuel cell. The theoretical maximum ratio of produced H₂ to methanol consumed is 2 for the POM reaction and 3 for the SRM reaction. For the CRM process under the conditions used in this study, the corresponding ratio is 2.6, i.e. significantly lower than for SRM. In addition, in CRM the reformat is diluted by nitrogen if air is used as oxidant (see Table 4).

CRM, however, provides an advantage over SRM as the reaction system can be made self-sustaining with respect to heat. Another drawback associated with the SRM system stems from the need for vaporisation of the additional water. This is an energy consuming step, keeping in mind that the heat of vaporisation (ΔH_{vap}) of water is higher than that of methanol:

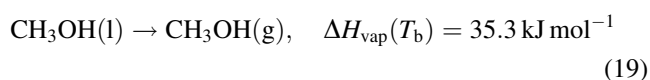
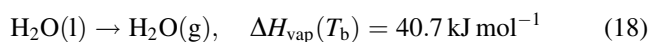


Table 4
Theoretical composition (mol%) of the reformat, assuming no by-products and full conversion of methanol and oxygen (H₂O/CH₃OH = 1.3; O₂/CH₃OH = 0.2)

Component	SRM	CRM (O ₂)	CRM (air)
H ₂	69.8	60.5	51.0
CO ₂	23.3	23.3	19.6
H ₂ O	7.0	16.3	13.7
N ₂	–	–	15.7

5. Conclusions

Production of H₂ by SRM was studied in the temperature range between 175 and 350 °C over a Cu/ZnO/Al₂O₃ catalyst from Süd-Chemie (G-66 MR). Methanol conversion was kinetically controlled in the lower temperature region, whereas mass transfer limitations occurred above ~ 220 °C. A kinetic model was fitted to the experimental data and used to simulate the production rates of CO₂ and H₂. The amount of catalyst or the temperature needed to obtain a certain conversion of methanol could also be predicted by the model. In general, a good correlation was found between the model and the experimental results and the model was able to quite accurately predict the rates of CO₂ and H₂ formation for a wide range of residence times. An Arrhenius-type function provided a good fit for the measurements of the rate constant $k(T)$ at temperatures below 220 °C and the calculated apparent activation energy (E_a) of 100.9 kJ mol⁻¹ agrees well with values reported in the literature. At higher temperatures, mass transport hindered the reaction kinetics and a fifth degree polynomial was used, instead of an Arrhenius expression, to describe the variation of the rate constant $k(T)$ with temperature. Changes in the experimental set-up, such as changing the particle size or optimising the feed composition, could help in avoiding potential mass transfer limitations.

Heat transfer is one of the main obstacles to overcome in the production of H₂ by methanol steam reforming. Addition of oxygen to the steam reforming process, so-called CRM, improves the heat balance and enables methanol reforming under close-to adiabatic conditions. In addition, the CO-level in the product is significantly lowered. The concentration of H₂ in the product, however, decreases due to dilution of the reformat. Essentially, addition of oxygen acts by increasing the steam–methanol ratio, as methanol combustion dominates at differential oxygen conversions. Hence, low CO-levels in the product are obtained. Keeping steam in excess of the amount required by the reaction stoichiometry is an effective means of avoiding CO formation at higher temperatures, by suppressing the RWGS reaction. The production of significant amounts of CO during SRM can be further avoided by operating under differential methanol conversions, at low temperatures and short contact times. There are several theories concerning the pathway for CO formation during steam reforming. The results obtained in this work support CO as a secondary product, formed by the RWGS reaction. Although complete elimination of CO in the methanol reformer seems all but impossible, the size and energy requirements of the clean-up step can be significantly reduced.

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References

- [1] V. Pour, J. Barton, A. Benda, Coll. Czech. Chem. Commun. 40 (1975) 2923.
- [2] J. Barton, V. Pour, Coll. Czech. Chem. Commun. 45 (1980) 3402.
- [3] H. Kobayashi, N. Takezawa, C. Minochi, J. Catal. 69 (1981) 487.
- [4] K. Takahashi, N. Takezawa, H. Kobayashi, Appl. Catal. 2 (1982) 363.
- [5] E. Santacesaria, S. Carrà, Appl. Catal. 5 (1983) 345.
- [6] J.C. Amphlett, M.J. Evans, R.F. Mann, R.D. Weir, Can. J. Chem. Eng. 63 (1985) 605.
- [7] C.J. Jiang, D.L. Trimm, M.S. Wainwright, N.W. Cant, Appl. Catal. A 93 (1993) 245.
- [8] C.J. Jiang, D.L. Trimm, M.S. Wainwright, N.W. Cant, Appl. Catal. A 97 (1993) 145.
- [9] J.P. Breen, J.R.H. Ross, Catal. Today 51 (1999) 521.
- [10] J.P. Breen, F.C. Meunier, J.R.H. Ross, Chem. Commun. (1999) 2247.
- [11] B.A. Peppley, J.C. Amphlett, L.M. Kearns, R.F. Mann, Appl. Catal. A 179 (1999) 21.
- [12] B.A. Peppley, J.C. Amphlett, L.M. Kearns, R.F. Mann, Appl. Catal. A 179 (1999) 31.
- [13] S.P. Asprey, B.W. Wojciechowski, B.A. Peppley, Appl. Catal. A 179 (1999) 51.
- [14] P.J. de Wild, M.J.F.M. Verhaak, Catal. Today 60 (2000) 3.
- [15] B. Lindström, L.J. Pettersson, Int. J. Hydrogen Energy 26 (2001) 923.
- [16] M.A. Peña, J.P. Gómez, J.L.G. Fierro, Appl. Catal. A 144 (1996) 7.
- [17] D.L. Trimm, Z.I. Önsan, Catal. Rev. 43 (2001) 31.
- [18] T.-J. Huang, S.-W. Wang, Appl. Catal. 24 (1986) 287.
- [19] T.-J. Huang, S.-L. Chren, Appl. Catal. 40 (1988) 43.
- [20] S. Velu, K. Suzuki, T. Osaki, Chem. Commun. (1999) 2341.
- [21] S. Velu, K. Suzuki, M. Okazaki, M.P. Kapoor, T. Osaki, F. Ohashi, J. Catal. 194 (2000) 373.
- [22] K. Geissler, E. Newson, F. Vogel, T.-B. Truong, P. Hottinger, A. Wokaun, Phys. Chem. Chem. Phys. 3 (2001) 289.
- [23] P. Mizsey, E. Newson, T.-B. Truong, P. Hottinger, Appl. Catal. A 213 (2001) 233.
- [24] S. Velu, K. Suzuki, M.P. Kapoor, F. Ohashi, T. Osaki, Appl. Catal. A 213 (2001) 47.
- [25] S. Murcia-Mascarós, R.M. Navarro, L. Gómez-Sainero, U. Costantino, M. Nocchetti, J.L.G. Fierro, J. Catal. 198 (2001) 338.
- [26] L. Alejo, R. Lago, M.A. Peña, J.L.G. Fierro, Appl. Catal. A 162 (1997) 281.
- [27] S. Velu, K. Suzuki, T. Osaki, Catal. Lett. 62 (1999) 159.
- [28] J. Agrell, K. Hasselbo, K. Jansson, S.G. Järås, M. Boutonnet, Appl. Catal. A 211 (2001) 239.
- [29] H.S. Fogler, Elements of Chemical Reaction Engineering, 3rd Edition, Prentice Hall, New Jersey, 1999.
- [30] M.V. Twigg (Ed.), Catalyst Handbook, 2nd Edition, Wolf Publishing, London, 1989.
- [31] M.S. Spencer, Nature 323 (1986) 685.
- [32] M.V. Twigg, M.S. Spencer, Appl. Catal. A 212 (2001) 161.