



Kinetics and modelling of dimethyl ether synthesis from synthesis gas

K.L. Ng^a, D. Chadwick^{a,*}, B.A. Toseland^b

^aDepartment of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, Prince Consort Road, London, SW7 2BY, UK

^bAir Products and Chemicals, Inc., 7201 Hamilton Boulevard, Allentown, PA 18195-150, USA

Abstract

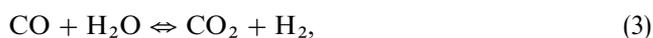
The kinetics of the dual catalytic methanol and dimethyl ether (DME) synthesis process over a commercial CuO/ZnO/Al₂O₃ (methanol forming) and a γ -alumina (dehydration) catalyst have been investigated at 250°C and 5 MPa using a gradientless, internal-recycle-type reactor. A kinetic model for the combined methanol + DME synthesis based on a methanol synthesis model proposed by Vanden Bussche and Froment (1996) *J. Catal.*, 161, 1–10) and a methanol dehydration model by Bercic and Levec (1993) *Ind. Engng Chem. Res.*, 31, 1035–1040) has been tested using results obtained from a wide range of CO₂:CO feed ratios. Results at different CO_x:H₂ ratio and catalyst loading ratios were also obtained. Catalyst deactivation was observed during DME synthesis at high space velocities and a large ratio of dehydration catalyst. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Methanol; Dimethyl ether; Kinetics; Modelling; Synthesis gas

1. Introduction

Synthesis of methanol, oxygenates, fuels and other hydrocarbon products from synthesis gas continues to be an area of both academic and industrial activity. These processes are also important for utilisation of remote natural gas or clean coal conversion. In this context, synthesis of dimethyl ether (DME), currently used as a propellant, has received growing attention owing to its potential as a useful chemical intermediate and its application as an alternative clean fuel (Toseland et al., 1994; Dybkjar and Hansen, 1997; Fleisch et al., 1997; Rouhi, 1995; Shi et al., 1996; Samdani, 1995). Direct synthesis of DME from syngas involves two steps, methanol synthesis followed by in situ methanol dehydration, Eqs. (1)–(4), which in turn requires two functionally independent catalysts, i.e. a methanol forming component and a dehydration component. An inherent advantage of the co-production of methanol and DME is the alleviation of the equilibrium limitation of the methanol synthesis (Peng et al., 1997), which results in a significant

increase in total methanol production.



Reactions (1)–(3) are catalysed by a methanol synthesis component (e.g. CuO/ZnO/Al₂O₃) and reaction (4) is catalysed by an acidic component (e.g. γ -alumina). Reactions (1)–(4) show a high degree of synergy provided the operating conditions are optimised such that the methanol produced is efficiently removed. Water formed in reaction (2) and (4) is removed via the water–gas shift reaction (3) to produce hydrogen which kinetically favours the production of methanol.

A wide range of possible feed and other operating conditions can be used in the combined synthesis process. The source of syngas, the type of reactor configuration, feed policy and the loading of the two functionally independent catalysts are closely interrelated. For example, the use of a CO rich hydrogen lean syngas derived from coal gasification is best suited to a CSTR configuration, such that in the liquid-phase di-methyl

* Corresponding author. Tel.: + 44 171 594 5579; fax: + 44 171 594 5604; e-mail: d.chadwick@ic.ac.uk.

ether process (LPDME) which provides good mixing and efficient heat management in the slurry-bubble column reactor. Additionally, the LPDME synthesis process also ensures that the catalyst system is exposed to a higher CO₂ content for the same syngas compared to the conventional fixed-bed-type reactor. Synthesis gas from natural gas can be converted either in a CSTR or fixed-bed reactor, but in this case the CO₂ management needs are different. A fixed-bed type reactor would suit a graded catalyst bed in which the methanol-to-dehydration catalyst ratio varied along the length.

Clearly, there is a range of plausible process variables which can be explored in the design of a combined synthesis process. However, the main focus of most published scientific literature has been on the catalyst development rather than the detailed kinetic work necessary to underpin the reaction engineering. The present study investigates some key process variables which influence the reaction kinetics of the dual catalytic methanol + DME synthesis process. Reported here are the effects of CO₂ feed concentration, CO_x/H₂ ratio and the catalyst loading ratio. This data have been used to test a kinetic model of the combined synthesis based on proposed models for the component reactions (Vanden Bussche and Froment, 1996; Chen et al., 1995; Bercic and Levec, 1992; Skrzypek et al., 1991). The kinetic work has been carried out in a continuous, internal-recycle reactor using a catalyst bed configuration in which a commercial methanol synthesis (CuO/ZnO/Al₂O₃) and a dehydration (γ -alumina, Norton) catalyst were physically separated, but exposed to the same, well-mixed, reaction environment such that the possibility of cross metal contamination between the two catalysts previously reported (Peng et al., 1997) was completely eliminated.

2. Experimental

Kinetics were measured in an internal recycle reactor (300 cm³ volume, 100 cm³ catalyst basket) at 5 MPa and 250°C using an impeller speed of 1500 rpm. For DME synthesis, the γ -alumina catalyst (supplied by Norton Chemicals Co.) and commercial CuO/ZnO/Al₂O₃ catalyst were crushed and sieved to size 250–500 μ m. The catalysts were stacked in two beds in the same catalyst basket, CuO/ZnO/Al₂O₃ on top of γ -alumina, with a layer of quartz wool physically separating them. The catalyst ratio of methanol forming and dehydration catalyst was typically 2:1 unless otherwise stated. The catalyst was activated in situ by reduction using a flow of 5% H₂ in N₂ at 250°C approached at 1°C min⁻¹ from room temperature for 12 h. Both internal and external particle diffusion resistance were confirmed absent. Two thermocouples were inserted central and at the bottom of the catalyst bed; a third was in the gas phase. The temperature difference between the thermocouples inserted into

the catalyst bed and the bulk gas phase was always $\pm 0.75^\circ\text{C}$ or less. This was in agreement with calculation which gave a temperature difference between the catalyst surface and the bulk gas phase of less than 1.0°C (Hougen, 1961 and Yoshida et al., 1962). The intraparticle temperature difference was calculated to be less than 0.5°C.

The required feed gas mixtures were obtained by blending a wide range of syngas compositions, CO_x:H₂ ratio = 1:1 to 1:4, (Air Products, CP grade) using a suite of mass flow controllers. 10% of helium was added as an internal analytical standard. The feed gas mixture was passed through a carbonyl trap (to remove Fe and Ni carbonyls) before entering the reactor. To avoid condensation of liquid products, the downstream line from the reactor was trace heated. A small fraction of the reactor effluent was piped to a GC for on-line analysis. Since hydrogen was used as the carrier gas, to utilise the He standard, hydrogen in the reactor outlet was not measured. The carbon balances of all experiments closed to 5% and in 90% of the experiments the balances closed to within 2.2%. The calculation of total methanol yield was based on the following:

Total methanol yield, Y_{TM}

$$= \left\{ \frac{n_{\text{CH}_3\text{OH}} + 2 \times n_{\text{CH}_3\text{OCH}_3}}{[n_{\text{CO}} + n_{\text{CO}_2}]_{\text{in}}} \right\} \times 100\%. \quad (5)$$

3. Simulation and parameter estimation

The simulation of methanol and/or DME synthesis reactions was based on a CSTR model. Several kinetic models for methanol synthesis and methanol dehydration reactions were tested (Vanden Bussche and Froment, 1996; Chen et al., 1995; Bercic and Levec, 1992; Skrzypek et al., 1991) under both independent and combined synthesis conditions. From the initial screening, the model for methanol synthesis proposed by Vanden Bussche and Froment (1996) based on a strictly sequential reaction mechanism of CO to CO₂ to CH₃OH via surface carbonate, and the dehydration model proposed by Bercic and Levec (1992) based on reaction of dissociatively adsorbed methanol, were selected for analysis and simulation of the combined process.

Parameter estimation was based on the minimisation of the objective function (6).

$$\min_{\theta} \Phi = \sum_{i=1}^I w_i^2 \sum_{k=1}^K (z_{ik,\text{pred.}} - z_{ik,\text{expt.}})^2. \quad (6)$$

Steady-state operation were modelled using gPROMS¹ (together with gEST) which utilised Eq. (6) and the mass

¹gPROMS, general PROcess Modelling system, is a software tool developed by the Centre for Process System Engineering at Imperial College. gEST, is an additional feature for parameter estimation.

conservation equations to determine the value of parameter θ that minimises the weighted, w_i , sum of the squares of residuals. The component balance equations used to construct the kinetic model were

$$F^o y_i^o - F y_i = W \sum_j [v_{ij} r_j]. \quad (7)$$

for all reactants, products and inert, with the exception of exit hydrogen for which no analysis was made. The methanation reaction was ignored. The kinetic rate equations, r_j , for methanol synthesis and dehydration were Eqs. (8)–(10).

$r_{\text{CO}_2 \text{hydrogenation}}$

$$= \left[\frac{k_1 (p_{\text{H}_2} p_{\text{CO}_2}) [1 - (1/K_{\text{eqm1}})(p_{\text{CH}_3\text{OH}} p_{\text{H}_2\text{O}})/(p_{\text{CO}_2} p_{\text{H}_2}^3)]}{(1 + K_2 (p_{\text{H}_2\text{O}}/p_{\text{H}_2}) + \sqrt{K_3 p_{\text{H}_2} + K_4 p_{\text{H}_2\text{O}}})^3} \right], \quad (8)$$

$$r_{\text{RWGS}} = \left[\frac{k_5 p_{\text{CO}_2} [1 - (1/K_{\text{eqm2}})(p_{\text{CO}} p_{\text{H}_2\text{O}})/(p_{\text{CO}_2} p_{\text{H}_2})]}{(1 + K_2 (p_{\text{H}_2\text{O}}/p_{\text{H}_2}) + \sqrt{K_3 p_{\text{H}_2} + K_4 p_{\text{H}_2\text{O}}})} \right], \quad (9)$$

$r_{\text{MeOH dehydration}}$

$$= k_6 K_{\text{CH}_3\text{OH}}^2 \left[\frac{C_{\text{CH}_3\text{OH}}^2 - ((C_{\text{H}_2\text{O}} C_{\text{DME}})/K_{\text{eqm3}})}{(1 + 2\sqrt{K_{\text{CH}_3\text{OH}} C_{\text{CH}_3\text{OH}} + K_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}}})^4} \right]. \quad (10)$$

4. Results and discussion

4.1. Methanol synthesis

Methanol synthesis was performed over the commercial CuO/ZnO/Al₂O₃ catalyst. Steady state was achieved within 24 h from start up and kinetic experiments were typically carried out over a duration of 100 h during which catalysts deactivation was insignificant, except when using a CO₂ free CO/H₂ feed. Fig. 1 shows the typical, steady state, activity profile of methanol (only) synthesis obtained by gradually replacing CO₂ with CO in the 1CO₂:4H₂ feed (e.g. Sahibzada et al., 1998). The maximum methanol production was obtained using synthesis gas with 2–5% CO₂, a common industrial feed condition. The methanol synthesis model, including the water–gas shift reaction, proposed by Vanden Bussche and Froment 1996 fitted our kinetic data reasonably well. A sensitivity analysis of the kinetics to parameters k_1 to k_5 , revealed that the adsorption constant of hydrogen, K_3 , strongly affects the magnitude and position of the local maximum at the low CO₂ content feed while the adsorption constants, K_2 and K_4 , mainly responded to feed conditions where high water concentration is found – for example in the CO₂ rich feed gas region. Methanol production is of course proportional to the magnitude of

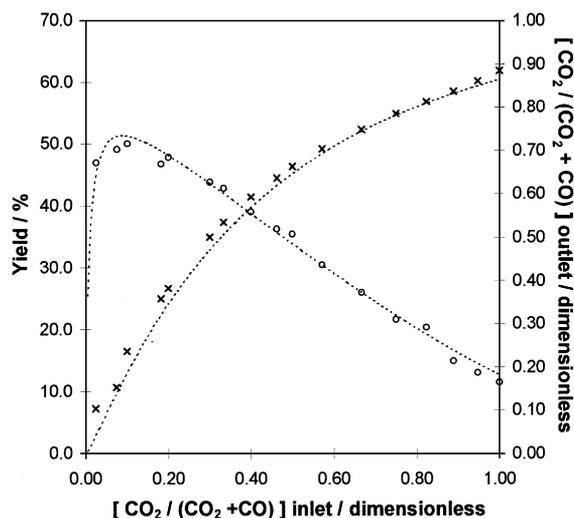


Fig. 1. Influence of feed CO₂ fraction on methanol yield and exit carbon oxide fraction in methanol (only) synthesis. (○) Methanol yield; (×) carbon oxide fraction in the outlet; (dashed line) – simulation results. Feed condition: CO_x = 18%, H₂ = 72% and He = 10%. Temp = 250°C, Press = 50 bar, GHSV = 27,500 h⁻¹.

reaction rate constant, k_1 , over entire range of different carbon oxide feed. Rate constant, k_5 , has only slight effect on the overall methanol production rate provided the shift reaction is sufficiently fast.

The parameters $B(i)$ were set to the values (Table 1) reported by Vanden Bussche and Froment, 1996, since the present study used a similar catalyst and was carried out at a single temperature. The data for a CO₂ free CO/H₂ feed gas were not included in the parameter estimation in the kinetic model due to the observed catalyst deactivation problem (Kung, 1992 and Klier et al., 1982). Only minor changes to the parameters of the original rate equations were required (Table 1). The solution was independent of the initial approximation of the parameters. Verification that the parameters in Table 1 were not bound dependent was achieved by varying the upper and lower bounds of the solution constraint for each of the parameters, k_1 to k_5 , over a wide range. Data dependence tests were performed by randomly excluding data points and by allowing for the error in the carbon balances. The results of this procedure showed variation in the estimated parameters of $\pm 3\%$, mainly affecting k_1 .

4.2. Dimethyl ether synthesis

Over the entire spectrum of feed compositions, calculation of chemical equilibrium showed that the overall methanol yield can be increased in principle by combining the methanol synthesis with the methanol dehydration reaction. Synergy in total methanol production is obtained by effective removal of the products from the methanol synthesis reaction, i.e. by minimising the

Table 1
Kinetic parameters for methanol synthesis

Parameters*	$A(i) \exp(B(i)/RT)$	
	$A(i)$	$B(i)$
k_1	1.65	36,696
K_2	3.61×10^3	0
K_3	0.37	17,197
K_4	7.14×10^{-11}	124,119
k_5	1.09×10^{10}	-94,765
K_{eqm1}	Twigg (1986)	
K_{eqm2}	Twigg (1986)	
K_{CH_3OH}	7.9×10^{-4}	70,500
k_6	3.7×10^{10}	-105,000
K_{H_2O}	0.84×10^{-1}	41,100
K_{eqm3}	Stull et al. 1969	

*See Eq. (8)–(10); values for $B(i = 1...5)$ are taken from Vanden Busche and Froment, 1996 and $B(i = 6, CH_3OH \text{ and } H_2O)$ from Bercic and Levec (1992).

reverse reaction. Consequently, maximum synergy is obtained close to the equilibrium limit for methanol synthesis where the reverse reaction rate is maximum. We demonstrate this point by comparing (see Fig. 2) the total methanol yield from methanol + DME synthesis to the yield from methanol (only) synthesis with increasing space velocity. The kinetics of DME synthesis were studied mainly at a space-velocity of $27,500 \text{ h}^{-1}$, which is sufficiently far from equilibrium conditions that the data are sensitive to the reaction kinetics of methanol synthesis, and close enough that synergy in DME synthesis is significant.

4.2.1. Influence of $CO:CO_2$ feed composition

It is of interest to explore the dependence of kinetics of DME synthesis on the CO_2 content of the feed gas to assist CO_2 management in the process, and to provide a suitable database for refinement of the DME model. Fig. 3 shows results obtained for methanol + DME synthesis using a 2:1 ratio of the commercial $CuO/ZnO/Al_2O_3$ catalyst to the γ -alumina. The simulated yield for methanol (only) synthesis over the same commercial $CuO/ZnO/Al_2O_3$ catalyst under the same conditions are included for comparison. In the dual catalytic synthesis, the characteristic maximum in the methanol production is not seen. Strong synergy in total methanol production is obtained using low CO_2 content feed in the combined synthesis process. Refinement of the rate and adsorption constants for the combined methanol + DME was restricted to the methanol dehydration model only, with the methanol synthesis simulated using the already modified rate Eqs. (8), (9) and Table 1. In the combined model it is assumed, therefore, that there was negligible adsorption of DME on the $CuO/ZnO/Al_2O_3$ catalyst. Modification of methanol dehydration was necessary to correct for the difference in catalyst activity. The activation en-

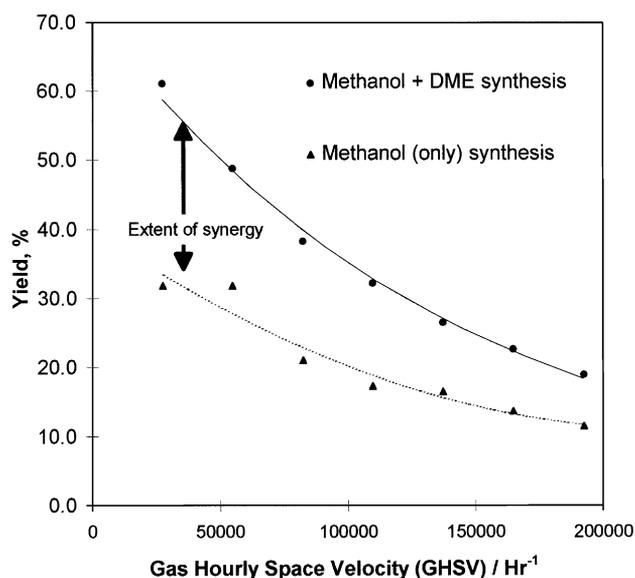


Fig. 2. Effect of gas hourly space velocity (GHSV) on total methanol yield. Feed condition: $CO = 18\%$, $H_2 = 72\%$ and $He = 10\%$. Temp = $250^\circ C$, Press = 50 bar.

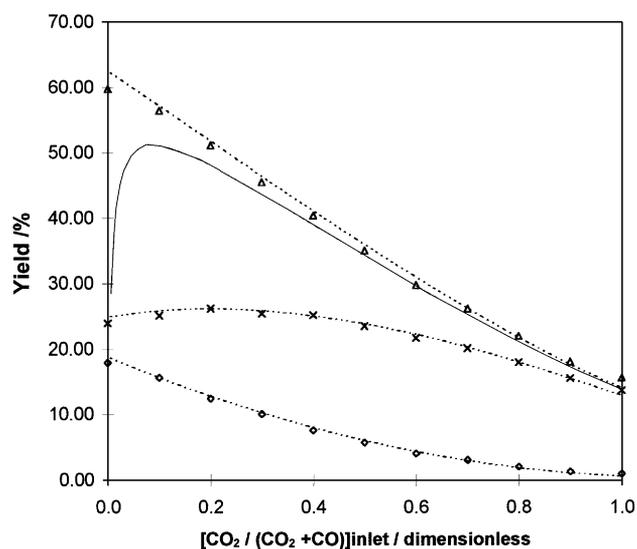


Fig. 3. Influence of feed CO_2 fraction on product yield in methanol (only) and combined synthesis. (Δ) Total methanol yield; (\times) actual methanol yield; (\diamond) DME yield; (dashed line) simulation results for combined synthesis; (solid line) simulation of methanol (only) synthesis. Feed condition: $CO_x = 18\%$, $H_2 = 72\%$ and $He = 10\%$. Temp = $250^\circ C$, Press = 50 bar, GHSV = $27,500 \text{ h}^{-1}$.

ergy in the original model (Bercic and Levec, 1992) was changed to 105 kJ mol^{-1} (increased by about 10%) to fit data obtained from separate methanol dehydration experiments at several reaction temperatures and low pressure (not presented here). The best-fit dehydration parameters to the combined methanol + DME synthesis are given in Table 1, where the heats of adsorption of methanol and water are assumed to be the same as those

reported by Bercic and Levec (1992). The slightly over estimated actual methanol yield may reflect a slightly lower catalyst methanol activity within normal experimental variation. The validity of the parameters given in Table 1 was tested by following a similar procedure to that described above for methanol (only) synthesis.

Results of both simulation and experiment show that at the present reaction conditions the total methanol yield is roughly three times higher than that of methanol (only) synthesis for the low CO_2 content syngas. The extent of synergy declined with increasing CO_2 feed concentration as expected. The strong synergy obtained with CO rich feed is due to the effective removal of methanol by dehydration and the product water by the water–gas shift reaction. In contrast, negligible synergy effect was observed at high CO_2 content where a relatively large amount of water is produced and the reverse water–gas shift reaction is favoured.

Selectivity to methanol or DME are always favoured at the two opposite extremes of feed composition. At CO rich end where the dehydration reaction is not affected by water, DME is favoured. At even lower space velocities, a higher selectivity to DME can be achieved. There was a high fraction of unconverted methanol at the high CO_2 end, Fig. 3, where the reverse water–gas shift reaction is favoured and dehydration reaction is inefficient due to strong water inhibition. This reinforces the fact that to achieve strong synergy between methanol synthesis and dehydration reactions requires efficient water removal via the water–gas shift reaction.

4.2.2. Influence of varying $\text{CO}_x:\text{H}_2$ ratio

The hydrogen content of syngas varies widely. For this reason, the influence of varying the $\text{CO}_x:\text{H}_2$ ratio on the performance of combined methanol + DME synthesis has been investigated. Typical industrial methanol synthesis feed conditions ($\text{CO} = 16.2\%$, $\text{CO}_2 = 1.8\%$, $\text{H}_2 = 72\%$ and $\text{He} = 10\%$) were first used and then the content of hydrogen was progressively reduced to pre-set $\text{CO}_x:\text{H}_2$ ratios by replacing H_2 with helium. The experimental results are shown in Fig. 4 together with the results of simulation using the parameters in Table 1. The total methanol and water production from both methanol (only) and combined synthesis processes is proportional to the concentration of hydrogen in the feed mixture. With increasing hydrogen feed concentration, selectivity to actual methanol is enhanced, while that of DME is reduced. This behaviour is simulated well by the refined model. The strong synergy obtained at the lower H_2 to CO_x ratio is attributed to the increasing ability to remove water via the water–gas shift reaction as noted above.

4.2.3. Influence of varying catalyst ratio

An important parameter in the design of a dual catalytic system is the catalyst loading ratio; that is the

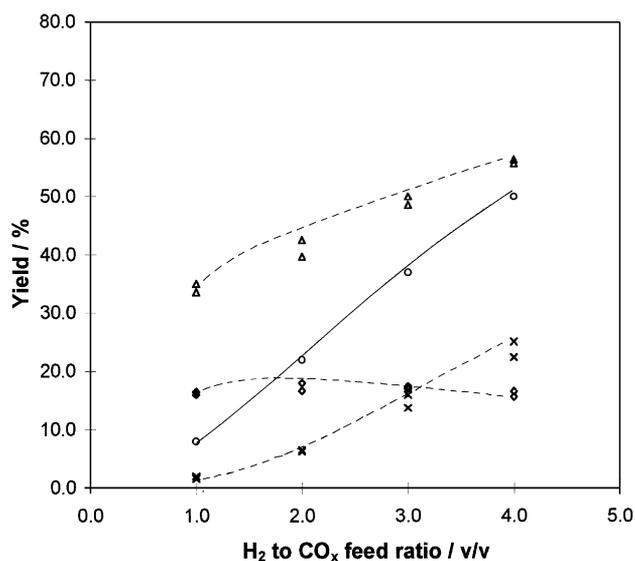


Fig. 4. Influence of feed CO_x/H_2 ratio on product yield in methanol and combined synthesis. (○) Methanol (only) yield; (△) total methanol yield; (×) actual methanol yield; (◇) DME yield; (dashed line) simulation results for combined synthesis; (solid line) simulation of methanol (only) synthesis. Feed condition: $\text{CO}_x = 18\%$, $\text{H}_2 = 72\text{--}18\%$ and $\text{He} = 10\text{--}72\%$. Temp = 250°C , Press = 50 bar, GHSV = $27,500\text{ h}^{-1}$.

methanol dehydration to methanol forming (and water–gas shift) activity. Too high a methanol dehydration activity compared to shift activity leads to a high water production. This aspect has been studied using four ratios of methanol synthesis-to-dehydration catalyst, i.e. 1:0, $1:\frac{1}{2}$, 1:1 and 1:2, using the same weight of $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst in each case. Results from the simulation predict an increasing total methanol yield and selectivity to DME as the ratio of dehydration catalyst rises, Fig. 5, reaching a rather constant level of total methanol production above a catalyst ratio of $1:\frac{1}{2}$. The experimental results are in good agreement with the simulation. However, at higher space velocities, we have noted that a maximum in total methanol yield occurs at a catalyst ratio of $1:\frac{1}{2}$, beyond which the total methanol production continues to fall with increasing loading of the dehydration catalyst. The deviation between the experiment and simulation is mainly caused by the actual methanol yield being lower than predicted. Close inspection of this result revealed that catalysts from runs conducted at high space velocity had suffered irreversible deactivation. This leads us to identify two counteracting factors: (i) the increasing synergy in total methanol production with a greater ratio of dehydration component and (ii) irreversible deactivation at high DME production. The results indicate that at higher space velocity the synergy effect is outpaced by the irreversible catalyst deactivation. Since catalyst deactivation in DME synthesis was not observed at the lower space velocity of $27,500\text{ h}^{-1}$, the results point to a gas composition

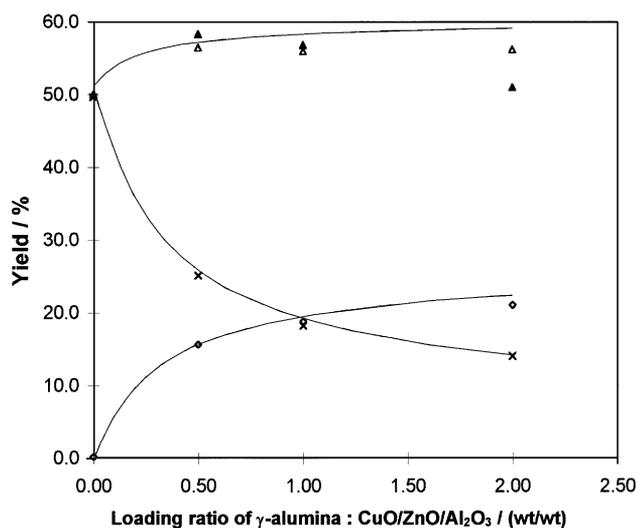


Fig. 5. Influence of catalyst loading ratio on product yield. (Δ) Total methanol yield; (\times) actual methanol yield; (\diamond) DME yield; (solid line) simulation results for the combined synthesis; (solid triangle) total methanol yield at higher space velocity (scaled by a factor of 1.62 for comparison). Feed condition: $\text{CO} = 16.2\%$, $\text{CO}_2 = 1.8\%$, $\text{H}_2 = 72\%$ and $\text{He} = 10\%$. Temp = 250°C , Press = 50 bar.

dependent deactivation process. Consequently, there is a need to improve the model of the combined synthesis by inclusion of a deactivation function to accurately simulate the synthesis process under all conditions.

5. Conclusions

A kinetic model for methanol and for methanol + DME synthesis based on a methanol synthesis model proposed by Vanden Bussche and Froment, 1996 and a dehydration model by Bercic and Levec, 1993, was found to agree well with experimental results over a range of CO_2 feed fractions. The refined model also simulated satisfactorily data obtained at different $\text{CO}_x:\text{H}_2$ ratios and catalyst loading ratios. At high yields, there was no evidence for inhibition of methanol synthesis by DME. However, deviation from the model of the combined synthesis was noted at high space velocity and large dehydration catalyst/methanol catalyst ratios. This effect is interpreted as evidence for a gas composition dependent deactivation process under some conditions.

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Notation

C_i	concentration of component i
F	molar flowrate at outlet, mol h^{-1}
F^o	molar flowrate at inlet, mol h^{-1}
k_i	reaction rate constants
K_i	adsorption constants
$K_{\text{eqm},j}$	equilibrium constant of reaction j
n_i	moles of component i in the outlet stream and
$n_{i,\text{in}}$	moles of component i in the inlet
P_i	partial pressure of component i
r_j	rate of reaction j , $\text{mol gcat}^{-1} \text{h}^{-1}$
w_i	weighted sum of the squares
W	weight of catalyst, g
y_i	mole fraction of component, i , at outlet
y_i^o	mole fraction of component, i , at inlet
$z_{ik,\text{expt}}$	k th value experimentally measured for variable z_i
$z_{ik,\text{pred}}$	k th value predicted for variable z_i

Greek letters

θ	unknown parameters
ν_{ij}	stoichiometric coefficient of component i involved in chemical reaction j

References

- Bercic, G., & Levec, J. (1992). *Ind. Engng Chem. Res.*, *31*, 1035–1040.
- Chen, Y., Sun, Q., & Ge, Z. (1995). *Chem. React. Engng Technol.*, *11*, 400–404.
- Dybkjar, I., & Hansen, J.B. (1997). *Nat. Gas Conv. IV*. In M. Pontes, R.I. Espinoza, C.P. Nicolaides, J.H. Scholtz, & M.S. Scurell, (Eds.), *Studies in surface science and catalysis*, 107, (pp. 99–103). Amsterdam: Elsevier.
- Fleisch, T.H., Basu, A., Gradassi, M.J., & Masin, J.G. (1997). *Nat. Gas Conv. IV*. In M. Pontes, R.I. Espinoza, C.P. Nicolaides, J.H. Scholtz, & M.S. Scurell, (Eds.), *Studies in surface science and catalysis*, 107 (pp. 117–121). Amsterdam: Elsevier.
- Hougen, O.A. (1961). *Ind. Engng Chem.*, *53*(7), 509–515.
- Jain, J.R., & Pillai, C.N. (1967). *J. Catal.*, *9*, 322–328.
- Klier, K., Chatikavaniij, V., Herman, R.G., & Simmons, G.W. (1982). *J. Catal.*, *74*, 343–353.
- Maureen Rouhi, A. (1995). *Chem. Engng News*, May 29, 37–39.
- Peng, X.D., Toseland, B.A., & Underwood, R.P. (1997). *Cat. Deact.* 1997, In C.H. Bartholomew, & G.A. Fuentes, (Eds.), *Studies in surface science and catalysis*, (pp. 175–182). Amsterdam: Elsevier.
- Sahibzada, M., Metcalfe, I.S., & Chadwick, D. (1998). *J. Catal.*, *174*, 111–118.
- Sam Samdani, G. (1995). *Chem. Engng*, April 1995, 17–19.
- Shi, R.-M., Cai, G.-Y., Liu, Z.-M., & Sun, C.-L. (1996). *J. Natural Gas Chem.*, *5*(4), 287–293.
- Skrzyppek, J., Lachowska, M., & Moroz, H. (1991). *Chem Engng Sci.* *46*(11), 2809–2815.
- Stull, D.R., Westrum, E.F., & Sinke, G.C. (1969). *The chemical thermodynamics of organic compounds*. New York: Wiley.
- Toseland, B.A., Underwood, R.P., & Waller, F.J. (1994). *Proceedings of 1994, DOE Contracts' Review Conference* (pp. 307–321).
- Twigg, M. (1989). *Catalyst Handbook* (2nd ed.), Wolfe Publishing Ltd, London, UK.
- Yoshida, F., Ramaswami, D., & Hougen, O.A. (1962). *A.I.Ch.E. J.*, *8*(1), 5–12.
- Vanden Bussche, K.M., & Froment, G.F. (1996). *J. Catal.*, *161*, 1–10.