KINETICS OF METHYL TERT. BUTYL ETHER SYNTHESIS IN GASEOUS PHASE

Alena HEJTMÁNKOVÁ, Karel JEŘÁBEK and Karel SETÍNEK

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchdol

Kinetics of methyl tert.butyl ether synthesis from methanol and isobutene was measured in gaseous phase at 85°C and atmospheric pressure on macroreticular ion exchanger catalyst containing strongly acidic functional groups SO_3H and on the same catalyst partially neutralized by sodium and iron ions. The form of the best Langmuir–Hinshelwood type kinetic equation suggests absorption of the reactants in the polymer mass causing "swelling" of it and influencing the accessibility of active sites by the reactants. Neutralization of the catalyst by metal ions suppresses this effect.

Synthesis of methyl tert. butyl ether (MTBE) catalyzed by strongly acidic organic ion exchangers is industrially important reaction producing a modern antidetonant gasoline additive. In industrial praxis it is performed under pressure maintaining all reactants in liquid state at reaction temperature. The ion exchanger catalyst swells in individual reactants to different extend. The composition of reaction mixture then influences not only the kinetics proper but also the accessibility of active centres[1–4]. Nevertheless, even at these conditions it is possible to describe the behaviour of the reaction using a simplified kinetic relation[5].

In gaseous phase, the swelling of the ion exchanger catalyst by absorption of reactants is much less significant than in liquid phase. Therefore, it is possible to assume that in such a case the results of kinetic measurements could be free of the influence of reactants on the structure of the ion exchanger catalyst.

We have measured the kinetics of MTBE synthesis from isobutene and methanol at 85°C and atmospheric pressure on an ion exchanger catalyst whose all active groups were in acidic form and on catalysts with a part active groups neutralized by sodium or iron ions. Kinetic data have been correlated by a set of Langmuir–Hinshelwood type equations and on the basis of obtained results the influence of the presence of neutralizing ions has been discussed.

EXPERIMENTAL

Materials. Methanol, ferric chloride, sodium hydroxide, all analytical grade (Lachema), isobutene, pure (Fluka) and nitrogen, (Technoplyn), were used as received.

Catalysts. The ion exchanger catalyst was prepared by sulfonation of a macroporous styrene-
-divinylbenzene copolymer with nominal divinylbenzene content 25%. The resulting ion ex-
changer had the size of particles $0.2-0.56$ mm, its surface area (BET) was 44 m^2/g with medium
pore diameter 44.5 nm and the exchange capacity was 3.81 mmol/g. This ion exchanger whose
all active groups were in H^+ form was designated MS-25. From it, other two catalysts were
prepared. In the first one, 10% of active groups were neutralized by sodium ions (MS-25(10%Na))
and in the second one 20% of active groups were neutralized by Fe^{3+} ions (MS-25(20% Fe)).
Weighed amount of ion exchanger MS-25 was wetted by distilled water and then the amount
of solution of the neutralizing compound (NaOH for MS-25(10% Na) and $FeCl_3$ for MS-25
(20% Fe)) corresponding to the desired degree of modification was added. The mixture was left
for 48 h to reach equilibrium and then the preparations were thoroughly washed with distilled
water and dried 6 h at 105°C.

Apparatus. An apparatus consisting of glass flow reactor covered with electric heating mantle
was used. Reaction temperature (85°C) was measured by a thermocouple located in a well in the
middle of the catalyst bed. Methanol was fed by a syringe pump into an evaporator heated to
115°C to which the streams of nitrogen and isobutene were brought in an desired molar ratio.
The output of the reactor was directly connected to the six-port sampling valve of the gas
chromatograph. The gas chromatograph was equipped with FID and the analyses were performed
at 113°C using a column 2 500 $\times$ 4 mm with Chromosorb W/AW + 25% Carbowax 20M as
the stationary phase.

RESULTS AND DISCUSSION

The kinetics of catalytic MTBE synthesis by addition of methanol to isobutene in
gaseous phase was investigated using the initial reaction rate method. It was verified
that at low conversions of isobutene (up to about 8%), the conversion was directly
porportional to the contact time. Hence, the initial reaction rate r^0 $(mol\ h^{-1}\ kg^{-1})$
was possible to calculate using the relation $r^0 = x/(W/F)$, where x is fractional
conversion of isobutene, W is weight of catalyst (kg) and F is isobutene feeding rate
$(mol\ h^{-1})$. It was also verified that in the whole range of reaction conditions used,
the course of the catalytic reaction was not influenced either by external or internal
diffusion effects.

During kinetic measurements, the ratio of partial pressures of methanol and iso-
butene was varied in the range from 9 : 1 to 1 : 20. Measurements were performed
on five levels of the sum of partial pressures of both reactants in the range $15-85$ kPa
adjusted by dilution of reaction mixture with nitrogen. At all reaction conditions
the only product of reaction was MTBE. On the catalyst MS-25, 32 values of r^0,
on catalyst MS-25(10% Na), 16 values of r^0 and on catalyst MS-25(20% Fe), 37 values
of r^0 were collected.

We attempted to correlate the kinetic data by Langmuir–Hinshelwood type equa-
tions using non-linear regression method based on Marquardt's algorithm[6]. It in-
cluded the minimization of the sum of squared relative errors Q_{rel}, defined by the
relation (*1*)

$$Q_{rel} = \sum[(r^0_{exp} - r^0_{theor})/r^0_{exp}]^2 \qquad (1)$$

in which r^0_{exp} are experimental and r^0_{theor} computed values of initial reaction rates.

For the correlation of the data obtained during experiments with the catalyst MS-25, a series of kinetic equations of the form (2) was wirtten.

$$r^0 = \frac{k p_m p_i}{[1 + (K_m p_m)^a + (K_i p_i)^b]^c},$$ (2)

k is the modified rate constant, K_m and K_i are adsorption coefficients, p_m and p_i are partial pressures. Indices m and i designate quantities corresponding to methanol and isobutene, respectively. Exponents a and b were varied in the range 0·5, 1 and 2 and exponent c in the range of integers 1−4. A relatively best correlation gave the values $a = b = 1$ and $c = 3$ but a satisfactory description of the experimental data was not achieved (dotted lines in Fig. 1a).

Substantial improvement was achieved only after a modification of the numerator of Eq. (2). In the numerator of Eq. (3)

$$r^0 = \frac{k p_m^x p_i^y}{[1 + (K_m p_m)^a + (K_i p_i)^b]^c}$$ (3)

the exponents x and y were treated as adjustáble parametes. This modification introduced into the model a possibility that the total number of active centres participating in catalytic reaction depends on the partial pressures of reactants.

In the course of further computations with various combinations of the exponents a, b and c, the values of the rate constant and adsorption coefficients and the values of exponents x and y were optimized. Like in the previous case, the equation in which $a = b = 1$ and $c = 3$ was found as suitable. The best values of exponents in the numerator were $x = 2·65$ and $y = 1·40$. It is possible to explain the high values of exponents x and y by a swelling of the polymer skeleton by absorption of methanol and isobutene vapours which increases the number of accessible acidic centres. It is possible to expect much stronger influence of methanol then isobutene in this process and with this corresponds higher value of exponent x then y.

The sets of data for catalysts MS-25(10% Na) and MS-25(20% Fe) were treated in a similar manner. Even in these cases, the best rate equation had $a = b = 1$ and $c = 3$. The resulting optimized values of adjustable parameters are shown in Table I.

It is known that the ability of polymer mass of acidic ion exchangers to swell in organic solvents is strongly suppressed by neutralization by metal cations[7]. Hence, the influence of neutralization of acidic groups of the ion exchanger catalyst by metal ions on values of the parameters of kinetic equation shown in Table I is an indication that during the MTBE synthesis, the surface of the catalyst swells due to the absorption of reactants even when the reaction is performed in gaseous phase.

The suppression of this effect by partial neutralization of acidic groups resulted in the diminishing of adsorption coefficients and exponents x and y. This behaviour contracts with results of the study of tert. butyl alcohol dehydration performed at

TABLE I

Optimized values of adjustable parameters in Eq. (3) for $a = b = 1$ and $c = 3$ for all ion exchanger catalysts

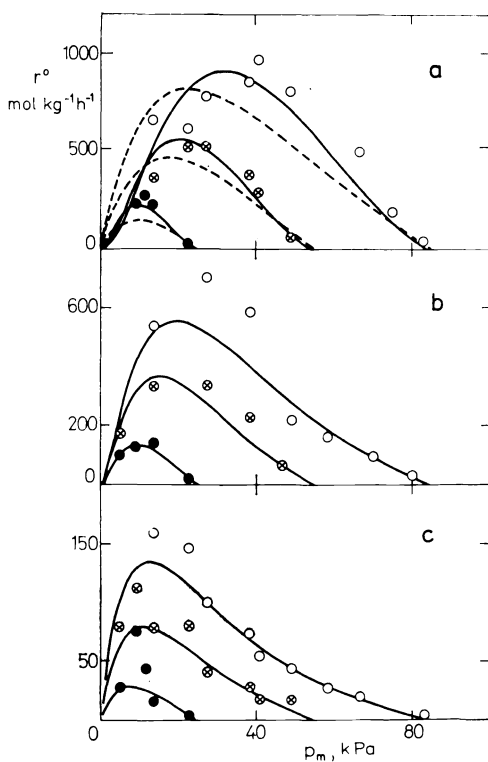| Ion exchanger	Parameter				
	k	K_m	K_i	x	y
MS-25	3·27	0·48	0·0077	2·65	1·40
MS-25 (10% Na)	0·83	0·076	0·0069	1·70	1·12
MS-25 (20% Fe)	0·41	0·031	0·0000	1·00	0·99

FIG. 1

Comparison of experimental and computed initial reaction rates r^0. Results on catalysts: a MS-25, b MS25(10% Na), c MS25(20% Ge). Sum of partial pressure of methanol and isobutene. ○ 85 kPa, ⊗ 55 kPa, ● 25 kPa (for simplicity are plotted only 3 from 6 levels of sum of pressures on which the measurements were performed). ——— Correlation by Eq. (3) ($a = b = 1$, $c = 3$, values of other constants shown in Table I). — — — Best possible correlation using Eq. (2) ($a = b = 1$, $c = 3$)

95°C where adsorption coefficients from a kinetic equation were found to be independent of neutralization degree of ion exchanger catalysts by potassium ions[8]. Differences in the character of the reaction kinetics of these two systems could be explained by better ability of methanol then butyl alcohol to swell the polymer mass of ion exchanger catalysts.

The present study of kinetics of MTBE synthesis in gaseous phase shows that even at the absence of a liquid phase the state of ion exchanger catalyst is substantially influenced by the absorption of reactants and therefore, the investigation of "pure" kinetics in which only adsorption of reactants on active sites participates is not possible.

REFERENCES

1. Ancillotti F., Mauri M., Pescarollo E., Romagnoni L.: J. Catal. *46*, 49 (1977).
2. Ancillotti F., Mauri M., Pescarollo E., Romagnoni L.: J. Mol. Cat. *4*, 37 (1978).
3. Muja I., Goidea D., Sandulescu D., Marculescu N., Andrescu G., Angehl G., Tomi P., Georgescu C.: Revista Chim. *33*, 10 (1982).
4. Gicquel A., Torock B.: J. Catal. *83*, 9 (1983).
5. Setínek K.: *Proc. 6th Int. Symp. Heter. Catal.*, p. 88. Ed. Bulgarian Academy of Sciences, Sofia 1987.
6. Marquardt D. W.: J. Soc. Ind. Appl. Math. *11*, 431 (1963).
7. Jeřábek K., Setínek K.: J. Mol. Catal. *39*, 161 (1978).
8. Jeřábek K., Bažant V., Beránek L., Setínek K.: *Proc. 5th Int. Congr. Catalysis, Miami Beach 1972*, p. 1193. North Holland, Amsterdam 1973.

Translated by the author (K.J.).