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THE OXIDATIVE DEHYDROGENATION OF METHYL ISOBUTYRATE TO METHYL METHACRYLATE

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Abstract

Oxidative dehydrogenation of methyl isobutyrate (MIA) mainly to methyl methacrylate (MMA) and methacrylic acid (MA) over an industrial oxidation catalyst designed for oxidation of isobutene to methacrolein ($Mo_{12}BiPMn_{3,5}Fe_3Mg_{3,5}K_{0,1}Si_{43}O_x$), and a solid heteropoly acid of the summary composition ($H_5Mo_{10}PV_2O_{40}$) at temperatures of 260 – 409 ^{0}C and pressure close atmospheric was studied. A time dependence of conversion of MIA over the oxide catalyst, as well as in case of heteropoly acid was possible to describe by the kinetic equation of the 1st order. However, only a low selectivity to MA and MMA was achieved with the oxide catalyst. Evidently, better results were obtained with the heteropoly acid catalyst. The relationship:

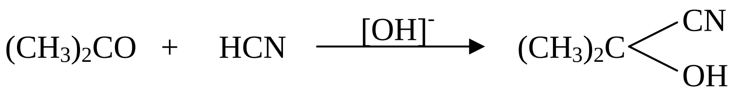
$$k = \left(1{,}41.10^6 \pm 2{,}55\right).\exp\frac{63236 \pm 168}{RT},$$

was found for the temperature range 530 – 685 K (*k* [$mol.dm^{-3}{}_{kat}.h^{-1}$]). From this relationship implies an activation energy *E* = 63,24 ± 4,68 $kJ.mol^{-1}$, activation enthalpy ΔH = 53,00 $kJ.mol^{-1}$ and activation entropy ΔS = -0,146 $kJ.mol.K^{-1}$. A selectivity to main products (MMA + MA) of about 60%, at temperature 290 – 320 ^{0}C (563 – 593 K), and catalyst load (with respect to MIA) of about 5 $mol.dm^{-3}{}_{kat}.h^{-1}$ and molar ratio O_2/ MIA = 1 was observed. Isobutyric acid (IA), diisopropyl ketone (DIPK) and carbon dioxide were registered as side products.

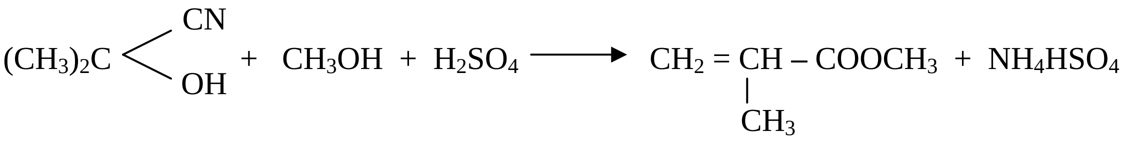
Beside experimental observations, mechanisms of main, parallel side and subsequent reactions, in the context of potential utilization of side products is discussed. Advantages of a rather simple heteropoly acid catalyst and its applicability for industrial scale are outlined. A new process of preparation of MMA from methylacetylene-alkene fraction of hydrocarbon pyrolysis, carbon monoxide and methanol is also analyzed.

***Key words:** isobutyric acid, methyl methacrylate, methacrylic acid, diisopropyl ketone, methanol, carbon dioxide, carbon monoxide, oxidation catalyst, heteropoly acid, kinetics, selectivity, propine, 1,2 – propadiene, carboxylic methylation.*

For a long time [1-3] it is industrially exploited process for the production of methyl methacrylate (an important monomer), which starts from acetone and hydrocyanic acid forming intermediate acetone cyanohydrin:

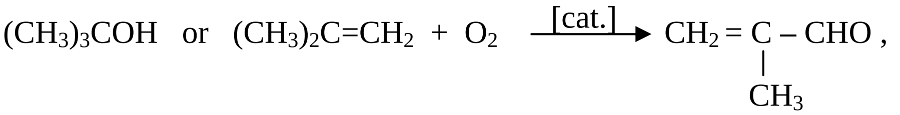


$$(CH_3)_2CO \quad + \quad HCN \xrightarrow{[OH]^-} (CH_3)_2C\begin{matrix} CN \\ OH \end{matrix} \qquad (1)$$



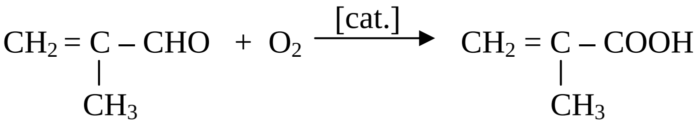
$$(CH_3)_2C(CN)(OH) + CH_3OH + H_2SO_4 \longrightarrow CH_2=C(CH_3)-COOCH_3 + NH_4HSO_4 \quad (2)$$

In a subsequent reaction, this intermediate is hydrolysed, dehydrated and reacts with methanol at presence of sulphuric acid, and MMA is formed. Just a toxicity of HCN and waste hydrogen sulphate are reasons for problems of this technology. Therefore, a two stage process started with oxidation of *tert*.butyl alkohol, or isobutylene with air or with pure molecular oxygen is of growing interest:



$$(CH_3)_3COH \text{ or } (CH_3)_2C=CH_2 + O_2 \xrightarrow{[cat.]} CH_2=C(CH_3)-CHO, \quad (3)$$

In the next, methacrylic aldehyde is oxidized to MA:

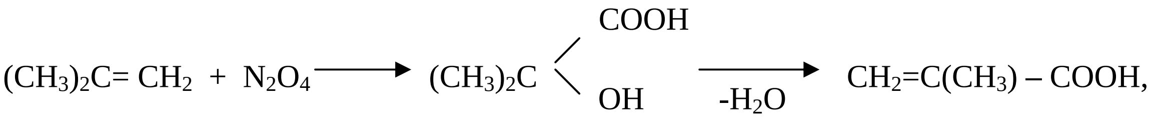


$$CH_2=C(CH_3)-CHO + O_2 \xrightarrow{[cat.]} CH_2=C(CH_3)-COOH \quad (4)$$

and in the 2nd step MMA is created by the esterification with methanol:

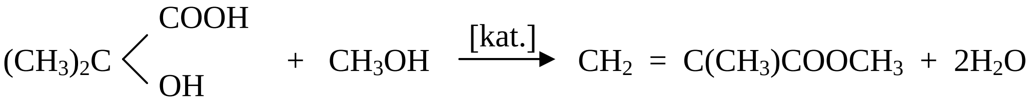
$$CH_2 = C(CH_2)COOH + CH_3OH \xrightarrow{[H^+]} CH_2 = C(CH_3)COOCH_3 \quad (5)$$

It is also possible to oxidize isobutylene with dinitrogen tetraoxide, which gives α - hydroxyisobutyric acid, and subsequently MMA is formed by elimination of water [1,3,4] (process Escambia [1]):



$$(CH_3)_2C= CH_2 + N_2O_4 \longrightarrow (CH_3)_2C(COOH)(OH) \xrightarrow[-H_2O]{} CH_2=C(CH_3)-COOH, \quad (6)$$

Elimination of water can proceed parallely with esterification [7-9] yielding MMA:



$$(CH_3)_2C(COOH)(OH) + CH_3OH \xrightarrow{[kat.]} CH_2 = C(CH_3)COOCH_3 + 2H_2O \quad (7)$$

Both the outlined new processes have been subjects of our investigation, whereas a row of original results [4-9] with potential industrial applicability was gathered.

In the context of oxo-synthesis of a mixture of n-butyr aldehyde with isobutyr aldehyde, which is prepared from oxo-syngas (CO : H_2 = 1 : 1) [1,11] and propylene, a “post-oxidation” of less valuable isobutyr aldehyde to isobutyric acid is worth of interest [3]:

$$CH_3CH(CH_3)CHO + O_2 \xrightarrow{[cat.]} (CH_3)_2CHCOOH, \quad (8)$$

Koch's hydrocarboxylation of propene at presence of strong acids is another possibility to prepare isobutyric acid [1,3,11,12]:

$$CH_2 = CHCH_3 + CO + H_2O \xrightarrow{[H^+]} (CH_3)_2CH - COOH, \qquad (9)$$

Even, hydrocarboxymethylation of propylene to methyl ester of isobutyric acid is possible [1,3, 1] :

$$CH_2 = CHCH_3 + CO + CH_3OH \xrightarrow{[H^+]} (CH_3)_2CHCOOCH_3, \qquad (10)$$

Subsequently, MA, and/or MMA may be prepared *via* oxidative dehydrogenation [3, 13] :

$$(CH_3)_2CHCOOCH_3 + O_2 \xrightarrow{[cat.]} CH_2 = C(CH_3)COOCH_3 + H_2O \qquad (11)$$

The most "oldest" dehydrogenation catalysts for this type of reaction are oxide compounds, namely that of Fe – Bi – P – Sb – Mo and others [13-19] . However, results of the oxidative dehydrogenation were not satisfactory for industrial purposes. A rather low selectivity to MA and MMA initialized investigations with heteropoly acids [20-23]. These catalysts are also suitable for a direct dehydrogenation of methyl ester of isobutyric acid [16,24,26].

A comparison of the industrial oxidation catalyst and phosphorous-molybdenum solid heteropoly acid in the oxidative dehydrogenation of methyl ester of isobutyric acid to MMA and MA is offered in this contribution.

Experimental

Chemicals and catalysts:

Methyl isobutyrate (methyl ester of isobutyric acid, MIA) with purity 99.8% wt.; b.p. = 92.6 ^{0}C/ 99.97 kPa; n_D^{20} = 1.3848; the content of water = 0.15% wt.

Methyl methacrylate with purity 99.1% wt. (without 1% wt. of hydroquinone as a stabilizer); b.p. = 100 ^{0}C/ 101.3 kPa; d_4^{20} = 936.0 kg.m^{-3}

Vanadium pentaoxide (Lachema, Brno, m.p = 690 ^{0}C/ 101.3 kPa.

Molybdenum trioxide with m.p. = 795 ^{0}C/ 101.3 kPa.

Trihydrogenphophorous acid water solution, 85% wt.; d_u^{20} = 1834 kg.m^{-3}

Nitrogen and oxygen - medical purity,

Other chemicals were of analytical grade.

Oxidation catalyst - industrial type of the compsition: $Mo_{12}BiPMn_{3,5}Fe_3Mg_{3,5}K_{0,1}Si_{43}O_x$, granulated with an average diameter of 4 mm and a height of 2.5 mm, S_{BET} = 142 m^{2}g^{-1}. The catalyst was activated in stream of nitrogen just prior to use for 1 h at 100, 200 a 300 ^{0}C.

Heteropoly acid type catalyst – $H_5Mo_{10}PV_2O_4$ was prepared from 238.5 g of MoO_3, 113.4 g of V_2O_5 and 11.4 g of H_3PO_4, which were put to a temperatured flask (5 dm^3) equipped with a stirrer and cooler. After addition of 3.2 dm^3 of distilled water and heating to 90 ^{0}C, the mixture was kept at this temperature under mild stirring for 20h. Then, a small portion of water was evaporated under a lowered pressure and black-red crystallites of heteropoly acid ($H_5Mo_{10}V_2PO_{40}$) were created. These crystallites were dried at temperature of 100 ^{0}C to a constant weight and a fraction of 0,8 - 4,0 mesh was isolated by sieving. Such a prepared catalyst was activated in a fixed bed reactor at temperatures of 100, 200 and 300 ^{0}C, while a residual water was released. The activated catalyst had a specific surface S_{BET} = 131 m^{2}g^{-1}.

Procedure for an oxidative dehydrogenation

Oxidative dehydrogenation of methyl ester of isobutyric acid (MIA) was carried out in a continuous apparatus with an integral reactor (i.d. 25 mm) and a volume of a catalyst either of 10 or 50 cm^3). The upper and down part of the reactor was filled with glass grains from the high temperature melting glass. These grains ensured heating of feeds (MIA, water, nitrogen oxygen). Heating of the reactor was with electric resistance wires in coat of the reactor and temperature was possible to control ± 3 ^{0}C. MIA, eventually water, was fed to reactor by a micropump. Nitrogen and oxygen were supplied from pressure flasks. A mixture of vapors and gases leaving the reactor was cooled and a liquid portion was separated. The proportion of liquids carried out in a gas was condensed in cooler traps at temperature –20 až -50 ^{0}C and a rest of vapors was absorbed in methanol cooled down with solid carbon dioxide to – 45 down to – 53 ^{0}C. All the solid and liquid raw materials and products were weighed or flow-rates of gas streams were measured. Temperatures in the reactor, as well as other parameters were registered in 5 – 15 min intervals.

Products were analyzed by the means of GC, using flame-ionization detector mainly. Some liquid products were analyzed for the content of elements and functional organic groups.

Results and Discussion

Industrial oxidation catalyst

In the first part of our investigations, we utilized the industrial oxidation catalyst ($Mo_{12}BiPMn_{3,5}Fe_3Mg_{3,5}K_{0,1}Si_{43}O_x$), which is mainly applied for the oxidation of propylene to acrylic acid. A study of the influence of temperature and catalyst loading is illustrated in Table 1.

Table 1: Influence of the reaction temperature (T) and catalyst loading (F/W) in the oxidation dehydrogenation of methyl ester of isobutyric acid (MIA) in stream of water, nitrogen and air, on the conversion (X) of MIA and selectivity to various products (V_{cat} = 10 cm^3 i.e. 7.5g, $Mo_{12}BiPMn_{3,5}Fe_3Mg_{3,5}K_{0,1}Si_{43}O_x$ catalyst, 2h lasting experiments.)

T ± 3 [^{0}C]	**Feed**				**F N_2+O_2 [Ndm^{-3}. h^{-1}]**	**F/W [mol. dm^{-3}. h^{-1}]**	**X [%]**	**Selectivity [%]**				**CO_2 in outgas [%vol.]**
	MIA		**H_2O**									
	[g. h^{-1}]	**[mol. h^{-1}]**	**[g. h^{-1}]**	**[mol. h^{-1}]**				**MMA**	**IA**	**MA**	**DIPK**	
303	21.8	0.21	42.5	2.40	45.8	21	14.3	0.18	51.7	10.2	1.8	0.08
325	21.6	0.21	43.0	2.40	46.7	21	23.0	0.22	57.6	13.4	3.4	0.20
350	21.2	0.21	44.5	2.50	45.1	21	30.3	0.34	61.1	14.2	8.5	0.65
379	22.1	0.22	41.6	2.30	45.3	22	40.8	0.62	44.1	16.9	13.6	1.21
386	21.7	0.21	46.1	2.61	45.0	21	49.3	0.73	43.1	16.1	13.6	1.22
364	14.3	0.14	37.4	2.12	38.7	14	42.9	0.55	69.2	16.3	11.0	1.41
360	21.7	0.21	37.6	2.10	41.8	21	33.4	1.0	82.4	8.9	7.6	1.22
362	25.6	0.25	37.5	2.11	44.0	25	31.0	1.0	76.1	6.8	12.1	1.03
361	30.6	0.30	35.3	2.00	47.2	30	26.7	1.4	72.1	4.4	21.1	0.94

MIA = methyl ester of isobutyric acid;
MA = methacrylic acid;
MMA = methyl methacrylate;
IA = isobutyric acid
DIPK = diisopropyl ketone

For treatment of kinetic data, we applied a kinetic equation [28] for a reaction of the 1st order and low desorption of reactants from the catalyst surface:

$$k = -\frac{F}{W}\left[2x + 3\ln(1 - X)\right], \qquad (12)$$

in which k = the rate constnt [mol.dm^{-3}.h^{-1}]; W = volume of the catalyst [dm^3]; F = feed [mol.h^{-1}]; X = conversion (% conversion : 100);

By treatment of log k *vs*. reciprocal value of the absolute temperature (1/T), a linear dependence was found, which confirms validity of the Arrhenius equation for the range of temperature 570 – 700 K:.

$$\log k = (6{,}463 \pm 0{,}426) - \frac{3394{,}09 \pm 505{,}0}{T} \ ,$$

$$\text{or:} \quad k = \left(2{,}91.10^6 \pm 2{,}67\right)\exp\frac{64987 \pm 505{,}5}{RT} \ ,$$

An activation energy E of 61.99 ± 3.06 kJ.mol^{-1} results from this relationship.

Applying theory [29] for deriving kinetic rate constant:

$$\log k = \log\frac{R}{N.h} + \log T - \frac{\Delta H^H}{2{,}300.RT} + \frac{\Delta S^H}{2{,}303.R} \qquad (13)$$

the following values for activation enthalpy and activation entropy were possible to calculate:

$$\Delta H^H = 59{,}78 kJ.mol^{-1}$$
$$\Delta S^H = -0{,}135 kJ.mol^{-1}.K^{-1}$$

It is evident from the obtained results (Table 1) that hydrolysis of MIA to isobutyric acid and methanol is mostly favored mainly as a consequence of presence of water:

$$(CH_3)_2CHCOOCH_3 + H_2O \rightleftarrows (CH_3)_2CHCOOH + CH_3OH \qquad (14)$$

Dehydrogenation and oxidative dehydrogenation of MIA to MMA and MA proceeds at a significantly lower extent:

$$(CH_3)_2CHCOOCH_3 \longrightarrow CH_2{=}C(CH_3)COOCH_3 + H_2 \qquad (15)$$

$$(CH_3)_2CHCOOCH_3 + \tfrac{1}{2} O_2 \longrightarrow CH_2{=}C(CH_3)COOCH_3 + H_2O \qquad (16)$$

$$(CH_3)_2CHCOOH + \tfrac{1}{2} O_2 \longrightarrow CH_2{=}C(CH_3)COOH + H_2O \qquad (17)$$

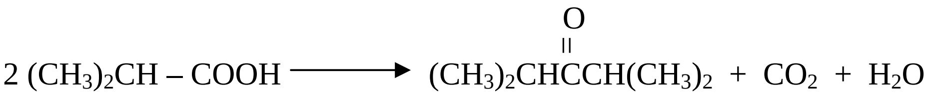
Analogically, hydrolysis of MMA to MA and methanol takes part:

$$CH_2{=}C(CH_3)COOCH_3 + H_2O \longrightarrow CH_2{=}C(CH_3)COOH + CH_3OH \qquad (18)$$

At relatively higher temperature, isobutyric acid is decarboxylated:

$$(CH_3)_2CH - COOH \longrightarrow (CH_3)_2CH_2 + CO_2, \qquad (19)$$

even diisopropyl ketone is formed:



$$2\,(CH_3)_2CH - COOH \longrightarrow (CH_3)_2CH\overset{\overset{O}{\|}}{C}CH(CH_3)_2 + CO_2 + H_2O \qquad (20)$$

Carbon dioxide can be originated by other transformations, too, e.g. total oxidation of isobutyric acid:

$$(CH_3)_2CHCOOH + 5\,O_2 \longrightarrow 5\,CO_2 + 5\,H_2O \qquad (21)$$

and others.

The low selectivity to MMA and MA is evidently connected with easy polymerization, which is even faster at temperature above 300 ^{0}C. Addition of 0.5% vol. of ammonia to fed air, for retardation of polymerization mainly, slightly increased the selectivity to MMA and MA (by 2 up to 4%), but still it is not sufficient for technological purposes.

It is very probable that addition of other more efficient volatile inhibitors would increase that selectivity; however such inhibitors would be of type not attacking the oxide catalyst.

To summarize the obtain results, it is possible to conclude that potentiality of this industrial catalyst for industrial process of production of MMA and MA seems to be very low not only as for selectivity, but also more expensive availability of raw materials makes this process non-perspective.

Heteropoly acid catalyst

Increasing interest for heteropoly acids, which are used not only for acid catalyzed reactions, but also for oxidation and oxidative dehydrogenation processes [16, 20 - 26], inspired us to prepare easy available heteropoly acid: $H_5Mo_{10}PV_2O_{40}$. This catalyst was tested for the oxidative dehydrogenation of MIA.

In comparison with previous experiments, a higher amount of the catalyst (50 cm^3 , 54 g) was used and dosage of water was excluded. Oxidative dehydrogenation was carried out with nitrogen-oxygen mixture. Obtained results with heteropoly acid catalyst are summarized in Table 2. In comparison with industrial oxidation catalyst, a higher conversion and selectivity to MMA a MA are evident. By increasing temperature from 260 up to 409 ^{0}C, conversion of MIA is also increased, but the selectivity to MMA is decreasing. In accordance with sequence of reactions, the selectivity to MA is increased at first and then remains virtually constant.

Table 2: Influence of the reaction temperature (T) and catalyst loading (F/W) of the heteropoly acid catalyst (50 cm^3 , 54 g) on the conversion (X) of MIA, the rate constant „k“ and selectivities to individual products after stabilization in 2h experiments.

T **± 3 [^{0}C]**	***F*** **(MIA)**		***F*** **N_2+O_2 [Ndm^3 h^{-1}]**	***F/W*** **[mol. dm^{-3}.h^{-1}]**	**Molar ratio O_2/MIA**	***X*** **MIA [%]**	***k*** **[mol. dm^{-3}.h^{-1}]**	**Selectivity [%]**				**CO_2 in outgas [%vol.]**
	[g.h^{-1}]	**[mol. h^{-1}]**						**MMA**	**MA**	**IA**	**DIPK**	
260	16.5	0.16	110.1	3.2	0.88	18.1	0.120	42.2	10.3	28.4	10.8	0.07
296	16.6	0.16	109.9	3.2	0.88	41.4	0.395	39.9	16.1	17.4	6.4	0.14
330	16.6	0.16	110.4	3.2	0.90	63.3	0.745	36.4	22.2	13.5	9.4	0.38
381	16.3	0.16	110.1	3.2	0.88	86.8	1.142	20.6	21.6	4.5	5.6	0.60
409	16.3	0.16	109.8	3.2	0.88	90.3	1.221	17.2	22.3	3.5	8.5	0.60
334	26.0	0.25	171.4	5.0	0.84	54.4	6.335	34.4	23.2	9.3	8.7	0.26
333	21.9	0.21	137.0	4.2	0.81	56.9	5.825	28.8	20.7	9.1	7.7	0.34
333	12.1	0.12	69.5	2.4	0.76	72.9	5.901	25.2	20.0	13.7	6.2	0.44
331	5.1	0.05	34.2	1.0	0.84	90.8	5.342	15.2	20.2	6.9	7.1	0.86

Validity of the kinetic equation (12) is confirmed not only by a linear shape of the regresion log *k* [mol.dm^{-3}.h^{-1}] *vs*. reciprocal *T* , but also by a relatively constant value independent of the catalyst loading (Table 2).

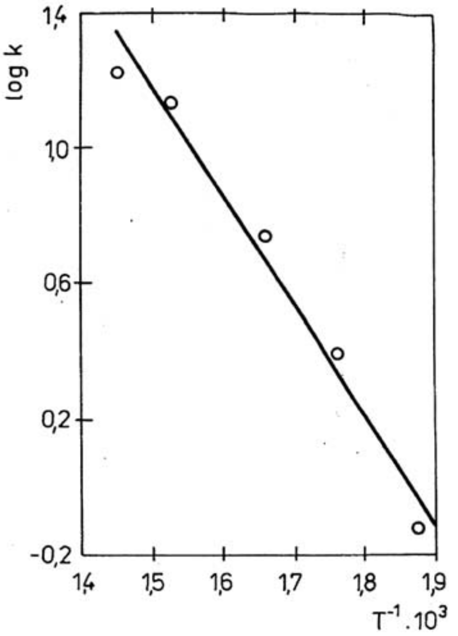


Fig. 1. Oxidation dehydrogenation of MIA. Logarithm of the rate constant
k [mol.dm^{-3}.h^{-1}] vs. reciprocal absolute temperature T [K]. of oxidative dehydrogenation MIA

“Arrhenius’s treatment” of the rate constant at various temperatures allowed gaining empirical equation:

$$\log k = (6{,}146 \pm 0{,}407) - \frac{3302{,}65 \pm 244{,}5}{T} \quad \boxed{\;,\;}$$

resp.

$$k = (1{,}41.10^{6} \pm 2{,}55)\exp\frac{63236 \pm 468{,}1}{RT} \quad [\mathrm{mol.dm^{-3}}_{\mathrm{kat}}\,.\,\mathrm{h^{-1}}]\,,$$

from which a value for activation energy E of 63,24 ± 4,68 kJ.mol^{-1} was estimated.

Similarly to procedure of treatment data for industrial oxidation catalyst, the activation enthalpy and entropy: ΔH^{H} =55,00 kJ.mol^{-1} and ΔS^{H} = -0,146 kJ.mol^{-1} , were calculated. Effect of temperature on the oxidation dehydrogenation is illustrated by Fig. 2, and influence of the catalyst loading is depicted by Fig. 3.

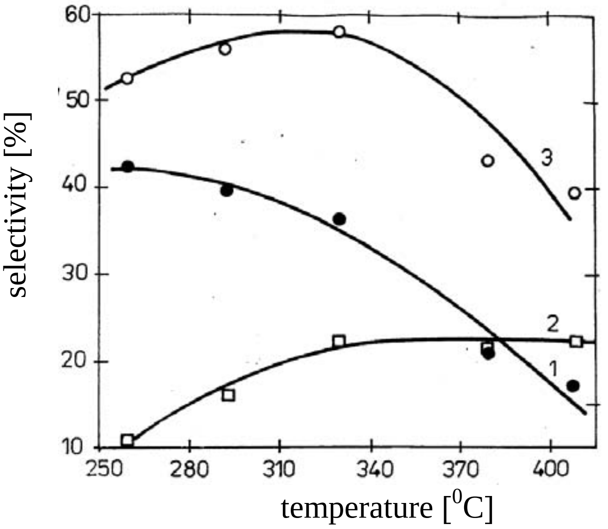


Fig. 2. Influence of temperature in the oxidative dehydrogenation of MIA on the selectivity to MMA (curve 1) and MA (curve 2). Curve 3 is sum of the formation of MMA and MA.

As in Table 2, Fig. 2 also depicts the selectivity to MMA, which decreased with increasing temperature from 260 up to 409 ^{0}C, and the selectivity to MA increases only slightly. Such a behavior implies a complex set of parallel and consecutive reactions, in which both reactant and products are consumed. The highest overall selectivity to MMA and MA (about 60 %) was achieved at 290 up to 330 ^{0}C.

While increasing loading of the catalyst with MIA, as given in Table 2, the conversion of MIA drops from 90,8 down to 54,4 %, but the selectivity to MMA increases gradually, and the selectivity to MA is increasing as well, i.e. the overall selectivity to MMA and MA from 20,2% at

1 mol.dm$^{-3}{}_{kat}$.h^{-1} up to 57,6% at 5.0 mol.dm$^{-3}{}_{kat}$.h^{-1}. Naturally, a higher contact time causes higher extent of side reactions, from which decarboxylation and oxidation are the main ones. Consequently, production of carbon dioxide is increased.

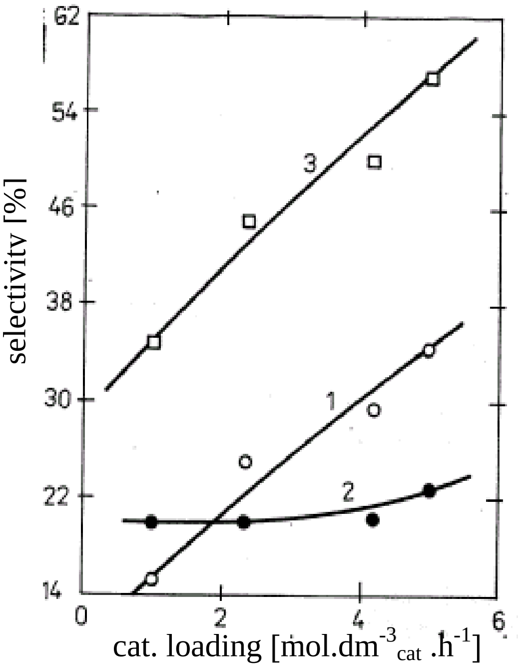


Fig. 3. Influence of the catalyst loading with MIA on the selectivity to MMA (curve 1), MA (curve 2) and to (MMA + MA) (curve 3).

Side reactions are also fairly documented by a higher formation of DIPK at a lower loading of the catalyst (higher contact time) – Fig. 4.

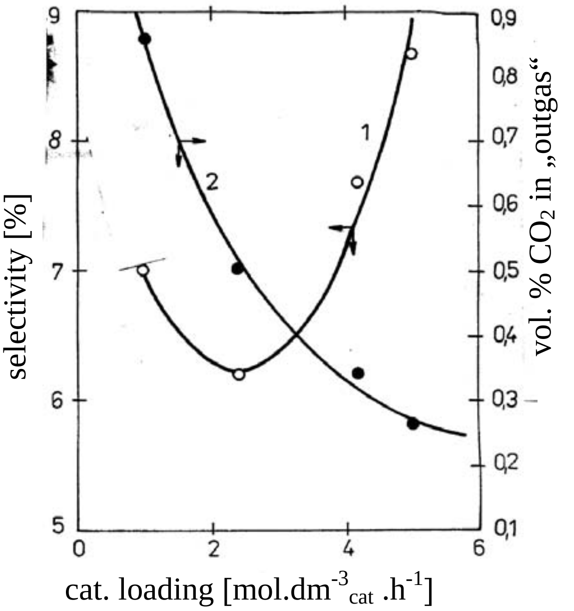


Fig. 4. Influence of the loading of the heteropoly acid catalyst with MIA at temperature 333 ± 2 ^{0}C and a molar ratio O_2/ MIA = 0,82 on the formation of DIPK (1) and CO_2 (2)

As a strong influence of the oxygen amount on the oxidative dehydrogenation is generally expected, we studied this. Results are in Table 2 and graphically interpreted in Fig. 5.

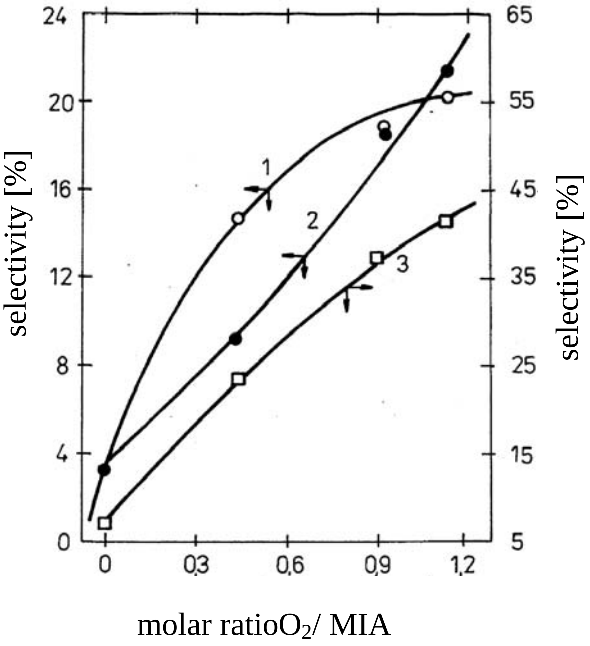


Fig. 5. Influence of the molar ratio O_2/ MIA on the selectivity to the formation of main products at a constant loading of the heteropoly acid catalyst with MIA (3,4 $mol.dm^{-3}_{cat}.h^{-1}$) and temperature 331 ± 3 ^{0}C. 1 – MMA; 2 – MA; 3 – MMA + MA

Increased selectivity to MMA and MA at increased molar ratio O_2/ MIA is evident from Table 2 and Fig. 5. The conversion of MIA at O_2/ MIA ≅ 0 (i.e. without an addition of oxygen), 0.43 and 0.92 was 41.6, 64.7 and 83%, respectively. This observation suggests that hydrolysis and dehydrogenation proceed without oxygen, while at O_2/ MIA ≅ 0.3 up to 1.13, oxidative dehydrogenation takes part mainly. Of course, main reactions are accompanied with other side reactions. However, it is still necessary to state that the overall selectivity to valuable MMA and MA of about 60%, even higher than on the commercial oxidation catalyst, is hardly accepted for industrial applications. The formation of DIPK should scarcely compensate significant extent of destructive reactions in which MIA and products are consumed, and invaluable carbon dioxide is formed.

A certain hope lies in lowering the acidity of heteropoly acid and investigations of other types of heteropoly acids, for example [16,19-26]. Optimization of main technological parameters is also a necessary step for improvement of the process.

It is worthwhile to mention a new [30,31] one-stage process of hydrocarboxylation and hydrocarboxymethylation of propine with carbon monoxide and methanol to MMA over a modified Pd – catalyst:

$$CH_3C{\equiv}CH + CH_3OH + CO \xrightarrow[\sim\ 100\ ^0C,\ 2\ MPa]{[cat]} CH_2{=}C(CH_3)COOCH_3 \qquad (22)$$

Methylacetylene (propine) is together with allene (1,2 – propadiene) a valuable component from the raw pyrolysis C_3 – fraction [3,30-32]. So far, this fraction is mainly treated by a selective hydrogenation to propene over a Pd – catalyst. The proportion of the propine and allene is about 50 kg per 1t of the produced ethylene, e.g., by pyrolysis of primary gasoline [32,33]. In addition, easy exploitation of this fraction is also underlined by a simple possibility to transform non-converted allene (1,2 – propadiene), or prior the reaction separated, it is possible to izomerize it [3,30, 31], over a strong-base catalyst to methylacetylene:

$$CH_2{=}C{=}CH_2 \xrightarrow{[K_2CO_3/\ Al_2O_3]} CH_3C{\equiv}CH \qquad (23)$$

Conclusions

The presented results show on non-suitability of the industrial oxidation catalyst $Mo_{12}BiPMn_{3,5}Fe_3Mn_{3,5}K_{0,1}Si_{43}O_x$, which is successfully applied for catalytic oxidation of propylene to acrolein, or isobutene to methacrolein, on the oxidative dehydrogenation of methyl ester of isobutyric acid to methyl methacrylate (MMA) and methacrylic acid (MA). Presence of water even decreased yields of these products.

Significant higher selectivities to MMA and MA were reached by the heteropoly acid catalyst ($H_5Mo_{10}PV_2O_{40}$) prepared in our laboratory. The overall course of oxidative dehydrogenation of MIA is possible to describe by the kinetic equation of the 1st order. The highest selectivity to MMA and MA (together of about 60%) was reached at 290 – 320 ^0C, catalyst loading of about 5 $mol.dm^{-3}{}_{cat}.h^{-1}$ and molar ratio O_2/ MIA ≅ 1. Side products were: isobutyric acid (IA), diisopropyl ketone (DIPK) and carbon dioxide.

Despite promising results achieved with heteropoly acid catalyst, obtained yields of MAA and MA are not satisfactory for development of large-scale technology. Better “tuned” acid catalysts are necessary to find. In any case, presented results indicate a route to oxidative dehydrogenation with heteropoly acid catalysts. Other known heteropoly acids are advised to test and stronger focus is necessary on the reaction conditions.

Heteropoly acids should be also of interest for other oxidative-dehydrogenation reactions, as well as for innovation of oxidation processes.

Other starting materials like propine and 1,2-propadiene are also very perspective for production of MMA and MA.

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