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A MACROKINETIC STUDY OF THE OXIDATION OF METHANOL TO FORMALDEHYDE ON Fe_2O_3 – MoO_3 OXIDE CATALYST

SIMION DRĂGAN[a*], IVETTE KULIC[a]

ABSTRACT. In this paper, a kinetic study about the oxidation of methanol to formaldehyde on Fe_2O_3-MoO_3 oxide catalyst was investigated. Results about the changes of the conversion at different contact times and the way the composition of the mixture respectively temperature influence the oxidation process, is submitted. The parameters were elected so that they match with those of the existing industrial reactors. We analyzed the influence of the above mentioned parameters on the rate of the process. Processing the experimental results in $\ln k - T^{-1}$ coordinates allowed the determination of the activation energy and the establishment of the corresponding mechanisms. The results, E_a=57.23 kJ/mol, indicate that under 520K the mass transformation processes (chemical reaction, adsorption – desorption) are the limiting ones the oxidation process. At temperatures higher than 535K the value of the activation energy, E_a=9.39 kJ/mol, emphasizes that limiting are the inner/outer diffusion phenomena. In the temperature range 520K – 535K, when E_a=25 – 42 kJ/mol, the process is carried out after a combined macrokinetic model (mass transfer –transformation).

Keywords: *methanol oxidation process, kinetic study, macrokinetic model.*

INTRODUCTION

Formaldehyde (FA) is a product of the organic chemical industry with many practical applications [1-3]. Big amounts of formaldehyde are used in the manufacture of ureo-, melamino- and fenaldehydical resins, which are used as adhesives or impregnating agents. The synthesizing of polyacetates and of 1,4-butandiol is based also on formaldehyde [4]. Another industrial branch which requires large amounts of formaldehyde is the production of fertilizers with the gradual solubility in time. Formaldehyde

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[a] *“Babeş-Bolyai” University, Faculty of Chemistry and Chemical Engineering, Arany Janos 11, RO-400028 Cluj-Napoca, Romania*

[*] *Corresponding author: sdragan@chem.ubbcluj.ro*

finds practical use also as a disinfectant of the agricultural lands or for the warehouses infected with pathogenic agents. In all these practical applications formaldehyde is used in the form of diluted solutions with a concentration of 38-40 %. World production of formaldehyde has an average annual growth rate of 3-4 % [2,5].

Formaldehyde has great importance in the economic since its production is in full development, what justifies the continuation of studies in order to improve its manufacturing technology.

The first industrial methods for formaldehyde synthesis used high purity methane gas as a raw material, which was oxidized on silver catalysts [6,7]. The high proportion of secondary reactions, the low yields in formaldehyde, the large and complicated installations for the purification of the product, made this procedure to have only historical importance. Over 90 % of the world production of formaldehyde is currently done after techniques which use methanol as a raw material [3,4], [6-10].

The production of formaldehyde from methanol was carried out in two different technologies which differ only in the used catalyst. In the first applied industrial method, the oxidation of methanol is performed on silver catalysts [9] at high temperature (500-600 °C) and pressure (1.3-1.5 atm.), in complex industrial systems, with large power consumption. The advantage of the method is the high concentration of methanol in the reaction mixture which defines less gas flow and higher concentration of formaldehyde in the final product.

The second method is based on the reactions discovered in 1931 by Adkins and Peterson [11] who oxidized for the first time methanol with molecular oxygen on Fe_2O_3 – MoO_3 oxide catalyst, in much milder conditions: range of temperature between 200-300 °C and atmospheric pressure. Although the process was industrialized since 1950, the composition of the catalyst remains almost unchanged up to the present time. Due to the economical efficiency of the method, did it to become more common on an industrial scale, therefore, studies have been reinforced for the improvement of the selectivity of the catalysts and of the industrial technology [12-20].

The studies for the improvement of the catalysts led to the conclusion that the catalytic activity and selectivity to formaldehyde are determined by the presence of two phases in the structure: a prevailing phase of $Fe_2(MoO_4)_3$ and one amorphous of MoO_3 located on the surface of the $Fe_2(MoO_4)_3$ spinel [21-26]. The presence of MoO_3 on the surface of the spinel is because it volatilizes during the operation, and facilitates the formation of Fe_2O_3, compound that catalyzes the oxidation to CO_2 [22-24, 27-29]. On the other hand Fagerazzi [30] shows that actually Mo^{6+} replaces Fe^{3+} in the crystalline network of the spinel and through this the catalyst retains both its activity and selectivity.

Massarotti [31] justifies the high activity and selectivity of Fe_2O_3 – MoO_3 catalyst trough the presence of MoO_3 dissolved in the dominant phase of the $Fe_2(MoO_4)_3$ spinel thereby providing the regeneration of the active surface.

As a result of the studies about the relationship between the catalytic activity, selectivity and the chemical composition of the catalyst, is established that the maximum activity for the $Fe_2(MoO_4)_3$ spinel corresponds to a Mo:Fe ratio of 1.5. In industrial practice the Mo:Fe ratio is 2.2-2.6 [28], the excess of Mo ensures a selectivity of 92-94 %, at a total conversion in methanol of 95-98 %.

The most of the worldwide conducted researches had as a goal establishing the causes what determines the deactivation of catalyst. It has been shown, that the deactivation is determined by the volatilization of MoO_3 [21-24], by the sintering [32-37] or forming of inactive Fe_2O_3 $FeMoO_4$ phases [22,23,33]. All phenomena what determines the deactivation of the catalyst are under the influence of the high operating temperature.

Obviously, many studies were made about catalysts used in the process but very little designed for the kinetic of the oxidation on industrial catalysts [12,21,38]. Productivity growth of the existing oxidation technologies of methanol to formaldehyde supposes, in addition to the improvement of the catalysts with the help of various additives of V_2O_5 and Co_2O_3 [12,38], the knowledge of the laws after which the overall process of oxidation is carried out, which is more complicated than the chemical reaction.

The overall process of oxidation must take into account, besides the mass transformation phenomena (chemical reaction, adsorption, desorption) those of internal and external diffusion [39-42]. Depending on the working conditions (temperature, concentration of the reactant mixture) the oxidation process of methanol to formaldehyde can be carried out after any of the possible macrokinetic models:

- mass transformation (chemical reaction, adsorption – desorption of reactants or of the reaction products);
- mass transfer of the reactants through the gaseous phase to the surface of the catalyst or of the reaction products from the surface in volume and diffusion through the pores of the catalyst;
- combined macrokinetic model mass transfer – transformation.

In this work a macrokinetic study is performed regarding the oxidation of methanol to formaldehyde on Fe_2O_3 – MoO_3 industrial catalyst in which we examined the effect of the reaction mixture and of the temperature on the global rate of reaction of the process.

RESULTS AND DISCUSSION

In order to highlight the influence of initial reaction mixture composition and temperature on the global rate of the oxidation process, measurements were conducted on which bases the conversion of methanol (Me) and the rate of oxidation, appropriate for different contact times, were calculated. The experimental results regarding the influence of the concentration of Me, O_2 and FA on the global conversion and on the oxidation rate of Me for different contact times are shown in fig. 1-6.

The data from fig. 1 underlines the strong influence of Me concentration in the reaction mixture on the global conversion. Thus, it is clear that at a content of 7.5 % vol. Me and 4 % vol. O_2 in the reaction mixture, the final conversion reaches the value of 70 % and increases till 84 % when the concentration of Me is reduced to 1.5 % vol. From fig. 2 it can be concluded that simultaneously with the reduction of Me content in the reaction mixture, the rate and rate constant of the oxidation process is decreasing, sinks from $1.35 \cdot 10^{-4}$ to $1.321 \cdot 10^{-7}$ mol/g·s·torr even though the excess in O_2 is growing from a ratio of O_2: Me=2.67 to O_2: Me=13.35. If we work with O_2 excess (over the stoichiometric ratio) the rate of the oxidation process does not depend anymore on the concentration of O_2, this only affects the final value of the conversion.

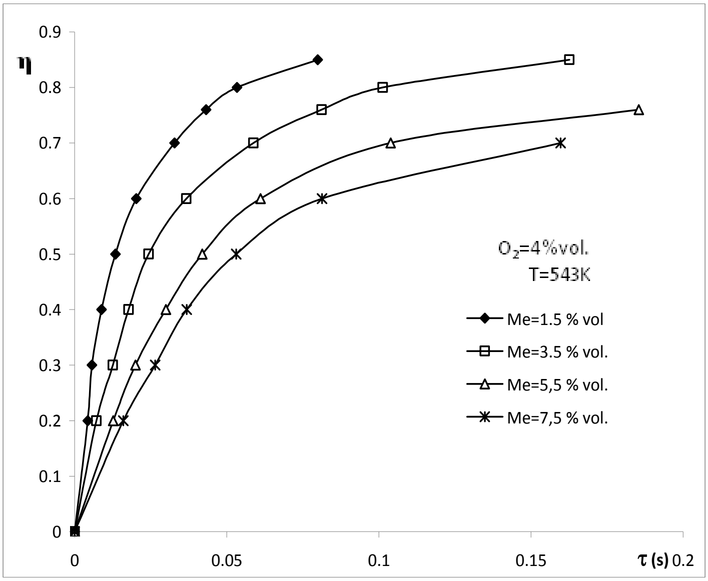

Fig.1. The conversion of methanol - contact time at different concentrations of Me

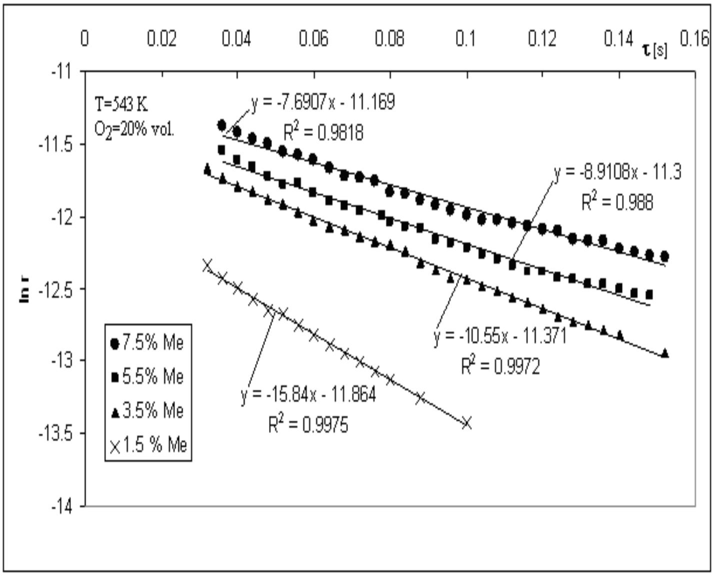

Fig. 2. The effect of concentration in Me on the rate of oxidation

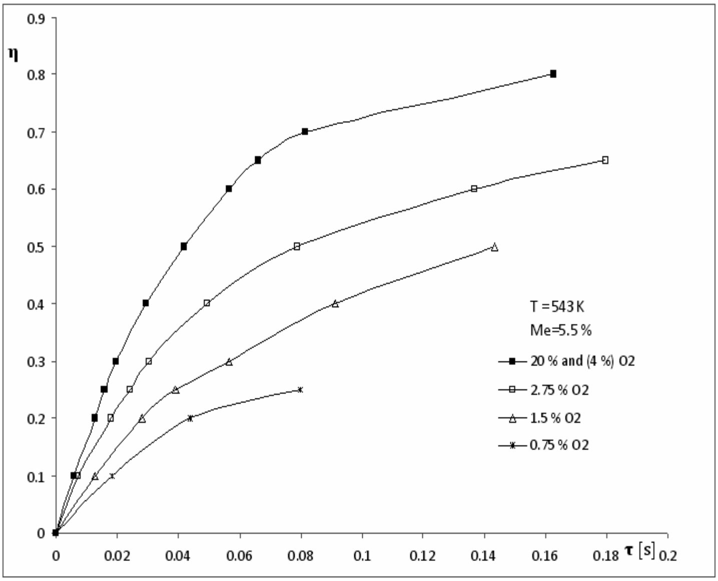

Fig.3. The conversion of methanol - contact time at different concentrations of O_2

In fig. 3 is presents the influence on the conversion of the O_2 concentration in the reaction mixture at a constant concentration of Me = 5.5 % vol. . There is a strong influence of the O_2 concentration (respectively of the ratio O_2:Me) in the reaction mixture over the conversion. At a ratio below the stoichiometric one (O_2:Me = 1:5) the final conversion of methanol barely reaches the value of 24 %. As the O_2 concentration increases (1.5 % vol.), which corresponds to a molar ratio of O_2:Me close to the stoichiometric one, the conversion increases significantly reaching the value of 50 %. When the concentration of O_2 equals the stoichiometric ratio O_2:Me = 0.5, more precisely 2.75 % O_2 in the reaction mixture, the conversion grows over 60 %. At a concentration of 4 % vol. O_2 which corresponds to a ratio O_2:Me = 4:5.5, the conversion of Me has a value around 80 %. It can be noticed that this value is identical with the conversion the corresponding to a great excess of O_2 in the reaction mixture (20 % vol. O_2) with a ratio of O_2:Me = 20:5.5.

In fig. 4 it is shows the influence of O_2 concentration over the oxidation rate.

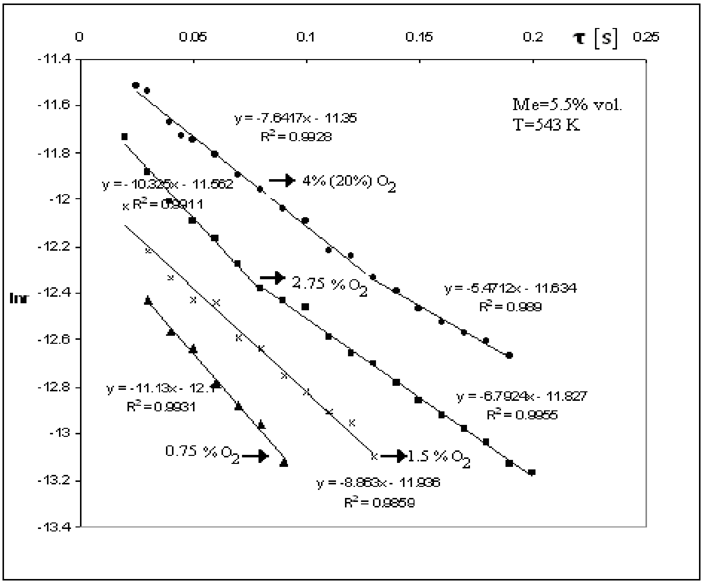

Fig.4. The effect of O_2 concentration on the rate of oxidation

At low concentration of O_2 in the reaction mixture (0.75 % vol.), which corresponds to a ratio of O_2:Me = 0.75:5.5, the angle coefficient is constant throughout the process and corresponds with the value of the rate constant equal with $k=1.466\cdot10^{-5}$ mol/g·s·torr. As the concentration of O_2 in the reaction mixture is growing, the rate and the rate constant of the process is increasing reaching at 1.5 % vol. O_2 a value of $1.415\cdot10^{-4}$ mol/g·s·torr. When the concentration of O_2 in the reaction mixture is 2.75 % vol. O_2 that corresponds to the stoichiometric ratio, it is seen that the points doesn't settle on one line. The rate constants for the two plots have the following values $3.28 \cdot 10^{-5}$ mol/g·s·torr, respectively $1.122 \cdot 10^{-3}$ mol/g·s·torr, which show that there is a change in the macrokinetic mechanism of the process. At concentrations of O_2 over the stoichiometric ratio the rate constants have higher values $4.80 \cdot 10^{-4}$ mol/g·s·torr, respectively $4.206 \cdot 10^{-3}$ mol/g·s·torr, indicating that also here we have a change in the macrokinetic mechanism, even if the excess of O_2 is much higher than the stoichiometric ratio O_2:Me = 20:5.5.

The Data in fig. 5 shows the influence of the FA concentration on the conversion. It is established that with the growth of the concentration of FA, the final conversion of Me decreases from 76 % (when the concentration of FA is 0 %) to 65 % (when the reaction mixture contains 6.3 % FA).

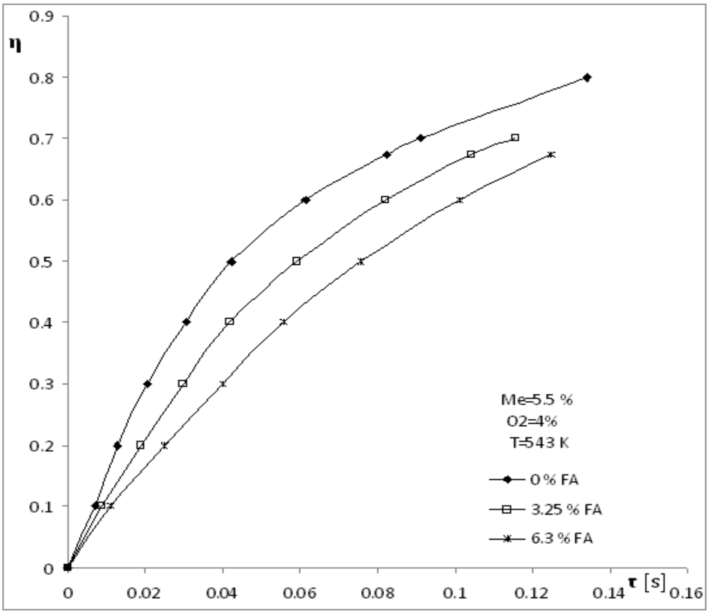

Fig.5. The conversion of methanol - contact time at different concentrations of FA

With increasing the content of FA in the reaction mixture, the reaction rate of the process is decreasing (fig. 6). At higher concentrations than 6.3 % vol. FA there is a change in the macrokinetic mechanism. The decrease of the oxidation rate with the growth of the FA content can be explained as follows: at high concentration of FA in the gaseous phase the driving force of the desorption process decreases and through this the normal movement of O_2 to the catalyst surface and the recovery of the $Fe_2(MoO_4)_3$ spinel is impeded, knowing that the oxidation is performed with O_2 from the spinel.

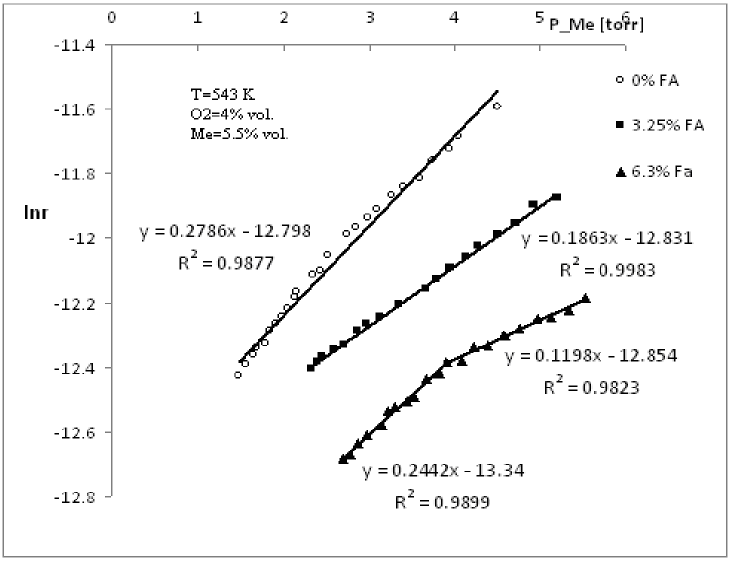

Fig.6. The effect of FA concentration on the rate of oxidation

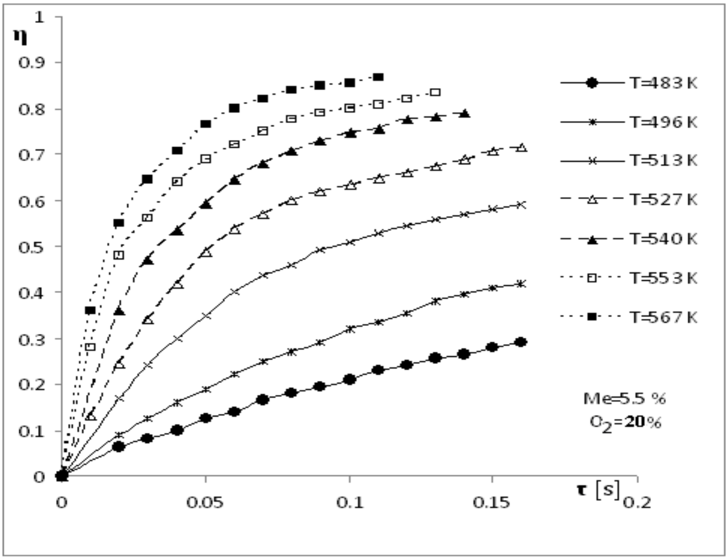

Fig.7. The conversion of methanol - contact time at different temperatures

As the temperature strongly influences the reaction rate, measurements were conducted, through which the influence of this parameter on the final conversion in the temperature range 475-567 K is revealed, which meets the working conditions of the current industrial reactors. The results are presented in fig. 7 and 8.

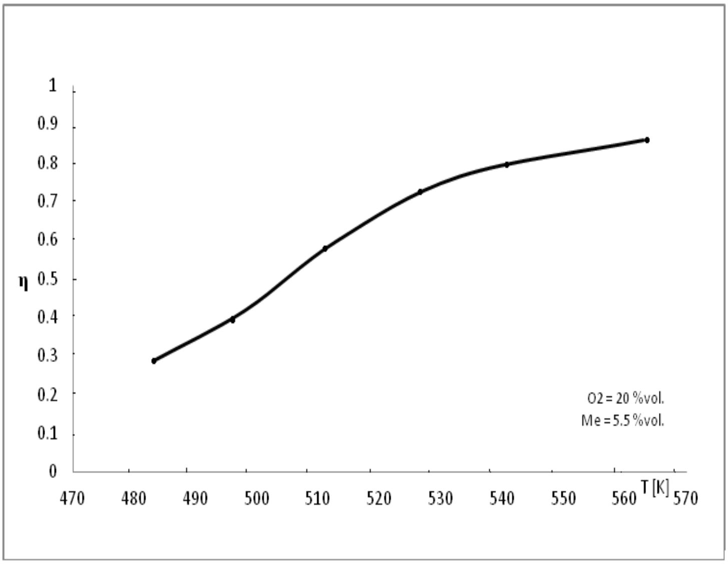

Fig. 8. The final conversion of Me at different temperatures

In fig. 7 it is seen that at temperatures under 513 K the conversion changes linearly with the contact time, reaching a value of 30 % at 475 K and increases until 55 % at 513 K. At temperatures above 513 K the conversion increases grows faster with the contact time to the value of 86 % at 567 K.

In fig. 8 we can see the change of the final conversion with the temperature at the same contact time. There is a linear increase of the conversion in the temperature range 475-500 K. After that the conversion increases faster, reaching a value of more than 75 % at 530 °K. Above this temperature, while maintaining approximately the same contact time as in the temperature range of 500-530 K, the final conversion continues to grow linearly to 85 % but with a significantly slight slope.

Table 1. The values of the rate constant

$k \cdot 10^7$ [mol/g·s·torr]	3.1	4.50	7.14	8.74	9.16	9.56	10.2
ln k	-14.989	-14.614	-14.152	-13.95	-13.903	-13.86	-13.796
T [K]	483	496	513	527	540	553	567

The graphical representation in $\ln r - T^{-1}$ coordinates of the data from table 1. is presented in fig. 9.

The diagram from fig. 9 shows a change in the slope around 515 K which leads to the conclusion that there is a change of the macrokinetic mechanism after which the oxidation process is carried out. From the slopes of the lines the activation energy was calculated. In the temperature range 475-515 K the value of the activation energy is 57.23 kJ/mol specific for the case when limitative are the mass transformation processes (chemical reaction, adsorption – desorption). In the temperature range 530 -567 K the activation energy has a small value, 9.39 kJ/mol, what suggests that limitative in this part of the process are the external or internal diffusion phenomena. It may also be noticed a narrow temperature region 530-540 K in which the value of the activation energy is in the range of 25-42 kJ/mol corresponding to a combined macrokinetic model: mass transfer – transformation.

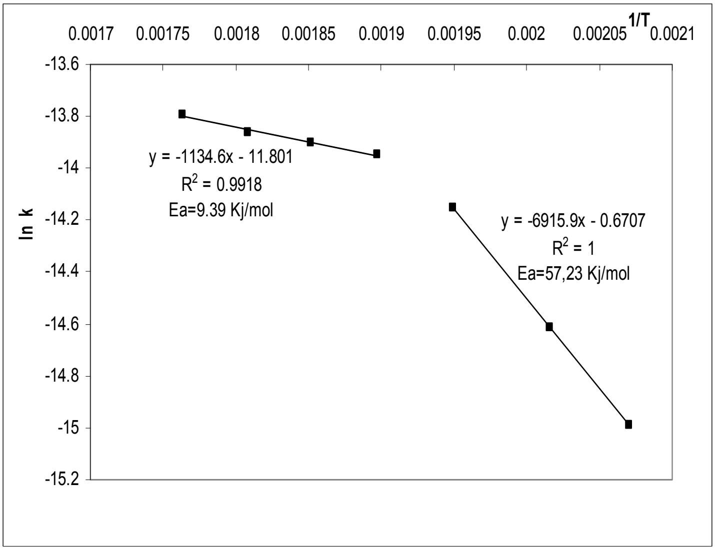

Fig. 9. $\ln\ \mathrm{k} - T^{-1}$ diagram

CONCLUSIONS

1. It was pointed out how the main parameters influence the conversion and the reaction rate.
2. It is noted that at a ratio of O_2:Me above the stoichiometric value neither the conversion nor the rate does depend on the concentration of O_2 in the reaction mixture.
3. The formaldehyde in the reaction mixture reduces significantly both rate and especially the conversion of Me.
4. The rate constants at different temperatures and from the $\ln k - T^{-1}$ diagram the activation energies were calculated.
5. It was pointed out that the process highly depends on the temperature being limited by the mass transformation phenomena under 518 K and by the external or internal diffusion phenomena above 523 K, which is indicated by the low values of the activation energy.

EXPERIMENTAL SECTION

The measurements were done on an industrial catalyst with the size of 5X5X2 mm and with the specific surface of 5.5 m^2/g determined by the BET method with nitrogen. The chemical composition of the catalyst corresponds to a ratio of Mo:Fe = 2.6 , the hole ratio and the density of the particle is $\varepsilon = 0.5$, respectively $\rho_{particol} = 1100$ kg/m^3. The reagents were of analytical purity: methanol of 94 % and formaldehyde solution of 38 % supplied by the company "Nordic". The used oxidizing agent was molecular oxygen from the air. For the achievement of necessary concentrations ratios, respectively, of the Me:O2 ratio was used N2 and O2 from cylinders. The effect of the temperature and of the reaction mixture (O_2, Me, FA) on the oxidation rate was examined in a reactor with recycle, with a diameter of 21 mm, made out of stainless steel put into an oven with automatic temperature adjustment. The formation of the reaction mixture Me–O_2, Me–O_2–FA was made by gurgling air through the saturator with Me respectively in two saturators: one for Me and another for FA. The heating of the mixture to the operating temperature was made in an oven with automatic adjustment. For a uniform distribution of the reaction mixture on the entire cross section of the reactor, the catalyst was covered with a 5 cm thick layer of inert material. The flow rate of the air, N_2 respectively O_2 was measured with a rotameter. The chemical composition of the output was determined using gas chromatography.

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