Thermodynamic Analysis of the Feasibility of Coupled Nonoxidative Dehydrogenation of Methanol into Formaldehyde

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Abstract—Thermodynamic and kinetic analysis of the reaction of nonoxidative catalytic dehydrogenation of methanol into formaldehyde was performed with the aim of developing a scientifically sound approach to the technology of the coupled process. With allowance for the experimental data, a kinetic model of the reaction was proposed and the feasibility of the occurrence of the process at low temperatures with the use of conventional catalysts and chemical coupling was shown.

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Coupled chemical reactions attract theoretical and experimental attention in relation to the development of nanotechnology and membrane catalysis. The reaction of methyl alcohol conversion, in our opinion, is a convenient model reaction which is expected to be accompanied by a variety of synergistic effects of induction and catalysis and is useful for simulating catalyst deactivation processes. A high activation energy of this reaction and the occurrence of a number of other undesired transformations under high-temperature conditions call for both the searching out of new catalyst systems and the employment of chemical coupling with the aim of reducing the temperature of the process and enhancing the selectivity.

The objective of this work was to develop a scientifically substantiated approach to the technology of coupled nonoxidative catalytic dehydrogenation of methanol. Such an investigation is also important from the standpoint of hydrogen economy in view that the nonoxidative dehydrogenation of methanol yields hydrogen [1, 2]. However, among numerous works reported in the literature on this issue, most studies are limited to the formal concepts of the process control principles.

The catalyst systems examined in the nonoxidative reaction of methanol dehydrogenation into formaldehyde were surveyed by Usachev [1]. Despite a wealth of information, there is still no sample of a catalyst for this purpose that holds promise for commercialization. Some systems, in particular zinc-containing heterogeneous catalysts, operate at a temperature that does not ensure the required minimum of energy input and at contact times and methanol partial pressures impractical for the use of these catalysts on the engineering basis. Other catalysts (e.g., sodium-containing systems) are not stable enough, and the presence of periodic regeneration steps in the process impedes the industrial use of these systems. In this connection, the development of catalyst systems continues, as well as the study of the reactor design philosophy.

The procedure for testing the catalytic activity of catalysts in the nonoxidative reaction of methanol dehydrogenation to formaldehyde is reported in [2]. The first results obtained on CaO–ZrO₂, SrO–ZrO₂, SiO₂, and firebrick catalysts are discussed there [2].

The catalyst K-1 used in this study is a SiO_2 -based model system which has a specific surface area of 10 m²/g and a bulk density of 0.7 g/cm³. Its selectivity and stability depend on the rheological properties, texture, and concentration of hydroxyl groups on the surface.

RESULTS AND DISCUSSION

The reaction of nonoxidative methanol dehydrogenation into formaldehyde is thermodynamically favored at high temperatures. Therefore, the selection of appropriate catalyst systems aims to reduce the activation barrier and to suppress side processes, above all, the carbon monoxide formation reaction. On the basis of thermodynamic analysis of the reactions [3, 4], it can be assumed that the formation of CO preferably follows the consecutive mechanism involving the degradation of formaldehyde:

> I CH₃OH = CH₂O + H₂, II CH₂O = CO + H₂.

The conclusion about the preferred successive degradation of the substrate results from the comparison of the enthalpies of the formation of carbon monoxide from methanol and formaldehyde. Judging by the values of the heat of formation for the products (see Table 1), it is obvious that the degradation of formaldehyde requires an order of magnitude smaller energy than methanol degradation.

<i>T</i> , °C	$\Delta H, J$							
	$CH_3OH \longrightarrow CO + 2H_2$	$CH_3OH \longrightarrow CH_2O + H_2$	$CH_2O \longrightarrow CO + H_2$					
900	105414.9	92720.4	12694.5					
950	105738.2	92905.8	12832.4					
1000	105982.7	93059.4	12923.3					
1050	106207.4	93235.6	12971.8					
1100	106464.2	93481.8	12982.4					
1150	106753.7	93794.5	12959.2					
1200	107076.3	94170.3	12906.0					

Table 1. Thermodynamic analysis of the heats of possible routes of nonoxidative dehydrogenation of methanol (thermodynamic calculation data)

In this context, the contact times need to be relatively short for the rapid withdrawal of the product formaldehyde from the reaction zone under the severe conditions of the process. Since an attempt to run the process at temperatures below 750°C led to a dramatic drop in the conversion and the turnover frequency of the conventional catalyst systems, it was necessary to find a nontraditional technical solution combining the advantages of the catalytic process with chemical coupling.

The reaction of nonoxidative dehydrogenation of methanol has a number of specific features characteristic of processes occurring in the non-steady-state region. A rapid drop in the activity of most catalyst systems proposed to date for the conventional methanol dehydrogenation reaction is due to the buildup of condensation products on the surface.

Owing to the specific structure of carbon monoxide [5], its formation reaction makes a significantly smaller contribution, as compared to the desired reaction, to the overall heat of the process (Table 1). The CO molecule is weakly polarized; thus, it blocks the sites responsible for sorption of other molecules, thereby affecting the acid properties, the concentration of hydroxyl groups, and, hence, the catalyst selectivity.

According to thermodynamic calculations [4], the probable products formed from 1 mol of methanol at 1000°C and atmospheric pressure in the absence of the catalytic effect are largely carbon monoxide and hydrogen in amounts of 0.986 and 1.969 mol, respectively. The formation probabilities for other products are 0.01 mol for methane and 6.5×10^{-7} mol for formaldehyde. At 750°C, no more than 31% of methanol can theoretically be converted with the CO yield an a passed-methanol basis of at most 26.8%. At 750°C, 0.63 mol of hydrogen, 0.27 mol of CO, 0.03 mol of methane, 2.27×10^{-5} % mol of ethylene, and 0.23×10^{-6} mol of formaldehyde are produced from 2.7 mol of methanol in accordance with the thermodynamics of the noncatalytic conversion of methanol. Consequently, the thermodynamically equilibrium yields are 23.3% hydrogen, 10% CO, 1.1% methane, 2.33×10^{-5} % ethylene, and $2.0 \times 10^{-5}\%$ formaldehyde. The selectivity of the process for CH_2O is $10^{-4}\%$. The main product is carbon monoxide.

Consider the mechanism of principal transformations in the system:



Scheme 1. Two-route graph.

This mechanism is represented graphically in scheme 1, in which the difference of the number of edges and independent key apexes determines two final cycles: 4 - (3 - 1) = 2. According to Horiuti's rule [6–12], 4 - 3 + 1 = 2 net stoichiometric routes also follow from the multistage scheme, which are determined by the difference of the number of steps and intermediates on the catalyst surface plus one steady-state condition expressed by the balance of concentrations of transient surface species (the sum of their fractions is unity).

In the presence of an appreciable amount of methane in the contact gas, the third route is actuated: III $CH_3OH + CO \longrightarrow CH_4 + CO_2$.

In this case, additional steps are observed:

5. $CH_3OH + ZCO \longrightarrow ZCH_4 + CO_2$,

6. $ZCH_4 \leftrightarrow Z + CH_4$,

and two edges and one apex associated to methane adsorption on the surface are added to the graph

(scheme 2): 6 - (4 - 1) = 3 cycles of the graph or three corresponding final stoichiometric routes. The scheme is correspondingly complemented by two steps and one transient surface compound CH₄Z.



Scheme 2. Three-route basis graph for the methanol conversion mechanism.

The matrix of stoichiometric coefficients for the participants of the reaction is given in Table 2.

The matrix rank (maximal number of nonzero minors [10]) is also 3. Thus, it is sufficient to know only three out of the six concentrations of the substances involved in the reaction; the others are determinable from the stoichiometric relationships. In the absence of methane and carbon dioxide from the matrix, its rank decreases to 2. Recall that the matrix rank determines a sufficient number of master parameters of the key substances taking part in the reaction. The choice of the key substances is arbitrary to some extent. Usually, one proceeds from the chromatographic limit of detection. For example, in the general case when all three routes are operative, the identical equimolar amount of CO_2 is found from the amount of methane; then, the number of moles of carbon monoxide equivalent to methanol conversion into methane is subtracted from the amount of CO detected in the contact gas. The amount of CO produced via the second route multiplied by 2 corresponds to the amount of hydrogen formed via this route. Then, the number of moles of hydrogen equal to that of the desired product (formaldehyde) will be determined by the difference of the total amount of hydrogen and its amount produced via the formal route. Comparing the formaldehyde concentration calculated by this algorithm with the amount of chromatographically detected formaldehyde (determination in the liquid aqueous product of catalysis-the amount of water in the formaldehyde scrubber is preset, 50 ml), it is easy to evaluate the accuracy of analytical determination.

In the absence of methane from the system, the task becomes easier and actually reduces to monitoring the concentration of two substances involved in the reac-

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Table 2. Matrix of stoichiometric coefficients for the substances participating in the reaction via net routes

Route	CH ₃ OH	H ₂	CH ₂ O	СО	CH ₄	CO ₂
Ι	-1	1	1	0	0	0
Π	0	1	-1	1	0	0
III	-1	0	0	-1	1	1

 Table 3. Theoretical mass balance for methanol-to-formaldehyde conversion, mol

Substance	Taken	Obtained
N ₂	1	1
CH ₃ OH	1	0.60
CH ₂ O	0	0.15
H ₂	0	0.15 + 0.50 = 0.65
СО	0	0.25
CH ₄	0	0
CO_2	0	0
Total:	2.00	2.65

tion. The determination of CO and hydrogen by gas chromatography only is practically sufficient in this case. Thus, the concentration of formaldehyde serves as a reference parameter for evaluation of the accuracy of analysis. In the case of good separation of methanol and formaldehyde, the task can be reduced to the determination of the gas composition on the basis of the compounds detected in the catalysis product. Then, knowing the methanol and formaldehyde concentrations, we calculate the concentrations of hydrogen and carbon monoxide (Table 3).

The number of moles in the system increases according to the stoichiometry (hydrogen formation via the main and side routes). In this case, 0.65 mol of hydrogen is additionally produced. Therefore, its amount changes from 2 to 2.65 mol. The volume correspondingly changes as well. The stepwise mechanism of the reaction to discuss the kinetics is given below (Table 4).

When the slow steps 1, 3, and 5 are chosen, the following rate equations are written for the steady-state conditions of the process:

$$\frac{d[X_2]}{d\tau} = k_1 P_1 - k_{-1} [X_2] P_4 - k_2 [X_2] + k_{-2} P_2 - k_3 [X_2] + k_{-3} [X_3] P_4 = 0,$$
(1)

$$\frac{d[X_3]}{d\tau} = k_3[X_2] - k_{-3}[X_3]P_4 - k_4[X_3] + k_{-4}P_3 = 0, \quad (2)$$

$$\frac{d[X_5]}{d\tau} = k_5[X_3]P_1 - k_6[X_5] + k_{-6}P_5 = 0, \quad (3)$$

Table 4.	Stepwise	mechanism	of methanol	conversion

Step	Stoichiometric number of steps by routes			
	Ι	Π	III	
1. $CH_3OH + Z \leftrightarrow ZCH_2O + H_2$	1	0	0	
2. $ZCH_2O \longrightarrow Z + CH_2O$	1	-1	0	
3. $ZCH_2O \longrightarrow ZCO + H_2$	0	1	0	
4. ZCO \leftarrow CO + Z	0	1	-1	
5. $CH_3OH + ZCO \longrightarrow ZCH_4 + CO_2$	0	0	1	
6. $\operatorname{ZCH}_4 \longleftrightarrow \operatorname{Z} + \operatorname{CH}_4$	0	0	1	

where P_1 , P_2 , P_3 , P_4 , and P_5 are the partial pressures of methanol, formaldehyde, carbon monoxide, hydrogen, and methane, respectively.

The concentrations of intermediates on the surface are denoted as follows:

It is meaningless to write the steady-state equation for the unoccupied surface area. First, at a low surface coverage, the concentration of these free islets appears to be raised to zero power (rate order). Second, even at a high or moderate coverage, for solving the inverse kinetic problem it is sufficient to use the additional steady-state condition, which relates all concentrations of transient surface intermediates by the mass balance equation at the established equilibrium:

$$[ZCH_2O] + [ZCO] + [ZCH_4] + [Z] = 1.$$
(4)

Solving the rate equations relevant to the two-route model with the specified slow steps results in the Langmuir-type equations:

$$W = K_1^* C_1 / 1 + bC_2, (5)$$

$$W_{\rm co} = K_2^* C_2 / 1 + bC_2, \tag{6}$$

where W and W_{co} are the methanol conversion and carbon monoxide formation rates, respectively; K_i^* are the apparent rate constants which are a combination of the rate constants of the elementary steps of the multistage scheme; b is the adsorption coefficient of formaldehyde; and C_1 and C_2 are the concentrations of methanol and formaldehyde, respectively. Note that the rate equations are derived on the assumption that the reac-

tion proceeds in the kinetic region.

In practice, it is necessary to make sure that there are neither postcatalytic transformations in the bulk nor interfering effects of external diffusion during the experiment. For this purpose, we compared the characteristics of the yield and selectivity for methanol at a fixed contact time, temperature, and methanol concentration and different charges (20 and 3 cm³) of crushed fused silica, which acted as a catalyst. It was found that the conversion changed at 900°C because of the contribution of side routes. Therefore, we decided to study the reaction kinetics at lower temperatures at which the contribution of destructive transformations is minimal. At 650–750°C, the yield of methane is practically insignificant and the concentration of carbon monoxide is an order of magnitude below that of the desired product. Preliminary experiments on varying the size of fusedsilica particles from 1.5 to 2.0 mm have shown that their size does not affect the characteristics of the process, thereby indicating noninterference of the internal diffusion effects and the occurrence of the reaction in a pseudo-steady-state kinetic region to which all of the above speculations about the kinetics are applicable. On the basis of the kinetic data (except those for the third route), the following first-order rate equations with respect to methanol and formaldehyde are derived for the methanol conversion and formaldehyde formation at low coverages:

$$W = K_1^* C_1, (7)$$

$$W_{\rm co} = K_2^* C_2.$$
 (8)

The formation rate for the desired product is described by the following equation in this case:

$$W_{\rm CH_2O} = W - W_{\rm co} = K_1^* C_1 - K_2^* C_2.$$
 (9)

At moderate surface coverages, we have

$$\left| W_{\rm CH_{2}O} = \frac{K_1^* C_1 - K_2^* C_2}{1 + b C_2} \right|.$$
(10)

Judging by the experimental data presented in Table 5, as the contact time increases over the temperature range 750–900°C in the reactor completely filled with fused silica (20 cm³), the destructive transformations of formaldehyde and parent methanol, which are clearly shown in the multistage scheme, are nonetheless manifested. Table 5 presents the results of the study of the nonoxidative reaction of methanol dehydrogenation on the model catalyst K-1. To attain a 50% conversion, large flow rates of nitrogen (inert carrier gas) and relatively high initial concentrations of methanol are required. However, a decrease in the temperature from 900 to 750°C leads to a substantial reduction in the yield of formaldehyde and an increase in the contact time leads to a reduction in the selectivity of the process.

From the mass balance of the process (Table 6), it is seen that hydrogen in the system accumulates in an amount that holds promise for use in the fuel lines of chemical plants. When the process is run selectively with a low yield of carbon monoxide, the amount of hydrogen formed substantially drops (Table 5) as a

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$W_{\rm CH_2O},$	T °C Catalyst	Nitro-	Methanol,	Methanol	Yield, %			Selectivity		
Run no.	g/((g cat) h)	1, C	charge, cm ³	l/min	ml/min	sion, %	CH ₂ O	СО	CH ₄	formaldehyde, %
1	0.141	900	3	0.326	0.35	85.4	1.8	83.6	~	2.1
2	0.315	750		0.326	0.335	23.5	4.16	19.34	~	17.7
7	1.19	900	20	1.4	2.8 (+5% H ₂ O)	45.4	12.6	32.8	~	27.7
8	2.02	900		0.7	2.8	50.5	21.3	29.2	~	42.3
9	1.59	900		0.7	2.8	48.0	16.8	31.2	~	35.0
20	2.12	900		1.4	5.6	40.6	11.2	25.9	3.5	27.7
3	0.06	750		0.326	0.335	30.0	5.0	15.0	10.0	6.0

Table 5. Effects of the temperature and the flow rate at different volumes of the K-1 catalyst (SiO₂) charge to the reactor on the characteristics of nonoxidative dehydrogenation of methanol

Note: The bulk density of the catalyst is 0.7 g/cm^3 , and the methanol density of is 0.79 g/cm^3 .

result of the specifics of stoichiometry of the two-route reaction.

The yield of formaldehyde, the selectivity of the process, and the conversion at 750°C were $B_{CH_{2}O} = 4.16\%$, $S_{CH_{2}O} = 17.7\%$, and $\alpha = 23.5\%$, respectively.

The high energy consumption impels investigators to search for new technical solutions. In particular, the problem can be resolved via interference with the prime reaction.

By definition [13], coupled reactions are a pair of reactions in which one reaction does not give products with a noticeable yield unless the other proceeds. If the coupling mechanism is known, the product yield from one of the reactions can be controlled by varying the conditions of the reaction in which active species are generated. Stoichiometric analysis of the possible model catalytic coupling of nonoxidative dehydrogenation of methanol, in particular, to the ethylene hydrogenation reaction, is demonstrated below.

In terms of experimental data on the nonoxidative dehydrogenation of methanol into formaldehyde, the mechanism can be predicted in the most general form in accordance with the basis of the net routes:

$$CH_{3}OH \longrightarrow CH_{2}O + H_{2},$$
$$C_{2}H_{4} + H_{2} \longrightarrow C_{2}H_{6}$$

$$CH_3OH + C_2H_4 \longrightarrow CH_2O + C_2H_6.$$

From the standpoint of thermodynamics, this interaction is feasible. In the region 500–900°C, the Gibbs energy change is $\Delta G < 0$.

However, chemical coupling differs from the thermodynamic one in that there is coupling of elementary intermediate events with the catalyst surface along with the contribution of the first and third routes to the for-

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mation of formaldehyde. It is the investigation of this inner mechanism that is necessary for the determination of possible mediators (surface intermediates common for both the main and the coupling reaction) responsible for the chemical coupling per se under catalysis conditions.

The use of acetone as an inductor of the desired transformation looks attractive at first sight, since isopropyl alcohol is supposed to form along with formaldehyde in this case. However, according to thermodynamic analysis, the Gibbs energy change ΔG is >0 in the given case and the probability that the process will be induced by acetone $(CH_3OH + CH_3COCH_3 - CH_2O +$ iso-C₃H₇OH) is close to zero. Our experiments have shown that the yield of isopropyl alcohol in the stoichiometric reaction with acetone does not exceed 1%, and an admixture of acetone has no effect on the main process of methanol dehydrogenation. In addition, the buildup of condensation products on the catalyst surface is considerably enhanced. Coke deposition during the nonoxidative dehydrogenation of methanol is one of the major problems associated with catalyst deactivation and non-steady-state conditions of the process. When ethylene is introduced, coke buildup leads to a

Table 6. Mass balance of the reaction (750°C, run 2)

Substance	Taken, g	Obtained, g	Obtained, wt %
CH ₃ OH	8	6.013	75.16
CH ₂ O	_	0.156	1.95
СО	-	1.593	19.91
H ₂	-	0.238	2.98
Total:	8	8	100%

dramatic drop in the selectivity after 10 min already (despite a significant increase in the yield of formaldehyde), thus requiring the subsequent regeneration of the catalyst in an air stream at 950°C for 3 h. In this context, it was necessary to find an optimal solution that would make it possible to run the process with a relatively long reaction cycle, retaining the known advantages of nonoxidative dehydrogenation over the oxidative process. This problem can be resolved in two fundamentally different ways. One is the trivial running of the process in the presence of oxygen introduced in substoichiometric amounts only to maintain the degree of surface oxidation required for retarding coke formation. The other, more effective solution in our opinion is conducting the reaction in the presence of hydrogen peroxide used as an inductor (at its low concentrations in the system) to generate hydroxyl radicals which mediate the chain process on the surface, as in the case of oxidative dehydrogenation of ethylbenzene to styrene [13] characterized by the same effect. Preliminary studies have shown that it is possible to reduce the temperature by 100°C and, simultaneously, to increase the yield of formaldehyde from 25 to 30-35%. However, these results need to be verified over long catalyst on-stream times and the catalyst surface should be modified with allowance for the effect of migration of hydroxyl radicals.

Thus, passing from oxidative dehydrogenation to the nonoxidative process, despite the well-known advantages associated with the possibility of formaldehyde production without the formation of a large amount of water is fraught with some difficulties. The main difficulties are relatively high reaction temperatures and a high extent of condensation of the products. Attempts to initiate the process with the use of coupled reactions in the presence of inductors, such as ethylene and ethane, failed primarily because of the unresolved problem of coke deposition on the catalyst surface during the process. In this connection, it seems that hydrogen peroxide as an inductor is a good choice for making chemical coupling practicable in the reaction of nonoxidative dehydrogenation of methanol into formaldehyde.

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