Problems of producing motor fuels from alternative raw materials*

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The mechanism and kinetics of reactions occurring in different processes of natural gas processing to motor fuels are considered. Among them are the syntheses of methanol, dimethyl ether, and gasoline from synthesis gas (syngas) and production of pure hydrogen from methanol. The general scheme of carbon-containing raw materials processing to produce motor fuels is considered using natural gas as example. The advantages of the direct synthesis of dimethyl ether (DME) from syngas (instead of methanol synthesis) over all processes producing motor fuels were shown. The synthesis of DME uses the syngas of almost any composition and, hence, the process scheme of carbon-containing feedstock → syngas → DME → gasoline becomes universal and appropriate for processing various raw materials. Prospects of using methanol as an easily transportable source of pure hydrogen were considered. The steam reforming of methanol is a reaction inverse to its synthesis. The oxidation of residual CO in order to purify hydrogen is favored in the mode of catalyst surface ignition. Modern catalysts and methods for removal of CO traces can provide production of pure hydrogen by methanol processing with an efficiency appropriate, in principle, for using the corresponding devices aboard a vehicle.

Key words: mechanism, kinetics; natural gas as motor fuel; syntheses of methanol, dimethyl ether, and gasoline; pure hydrogen from methanol.

Introduction

An interest in processes for production of motor fuels from alternative raw materials has sharply increased because of restricted oil resources and other factors resulting in local fluctuations of oil prices. Predictions of the 1980s, according to which the cost of the synthetic fuel should be equal to that of the fuel of petroleum origin to the 2000—2005, are likely invalid. The cost of the synthetic liquid fuel is still much higher than that of the petroleum fuel. Therefore, the corresponding processes are not widely used so far in industry, even where the labor force and coal are still cheap. These processes can be renewed only by basic improvements of the component stages. Such improvements appear, in turn, due to fundamental studies of the kinetics and mechanism of occurring reactions and/or drastically novel technological solutions.

In this work, we considered the kinetics and mechanism of particular reactions occurring under conditions of natural gas processing and some possibilities of improving the technology on the basis of information obtained by these studies. In particular, the syntheses of such energy resources as methanol, dimethyl ether, gasoline (through dimethyl ether), and hydrogen for fuel cells (purified from CO traces) are described, and the role of these reactions in the system of synthetic fuel production is revealed (Scheme 1). The total array of methods for carbon-containing feedstock processing to motor fuels is shown using the natural gas as example. These processes are valid for other types of raw materials, as the changes are only in the stage of syngas production.

At the first stage, natural gas or other raw material is converted to a more reactive syngas (mixture of carbon oxides, predominantly, CO and hydrogen). Alternative directions of the second stage are the Fischer—Tropsch synthesis (FT) and synthesis of methanol and/or dimethyl ether (DME). The latter, in turn, can be transformed into high-octane gasoline and used directly as a motor fuel or fuel additives. A relatively new direction is the use of methanol and/or DME as a hydrogen source for hydrogen energetics. In principle, hydrogen can be used in vehicles as an energy source, which seems promising, at least, from the ecological point of view. However, in this case, one has to choose appropriate "hydrogen sources" and produce pure hydrogen from them with a high efficiency that allows one to place the corresponding apparatus under the automobile hood.

According to the aforesaid, let us consider the syntheses of methanol, dimethyl ether, and gasoline from

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* The materials of the report at the III International School "Engineering Chemical Science for Advanced Technologies" [1] and recent publication[2] were used in part.

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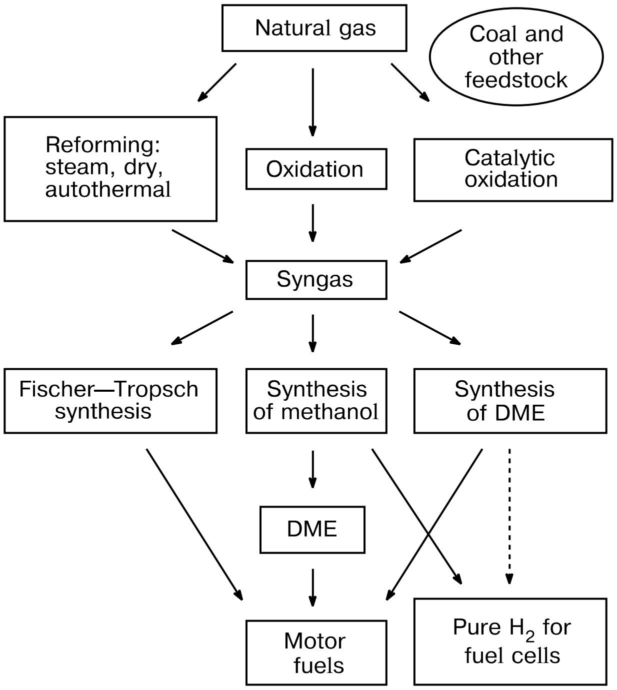
Scheme 1



syngas and the production of pure hydrogen from methanol.

Fischer—Tropsch synthesis makes it possible to obtain hydrocarbons from syngas in one stage and, hence, has intensely been studied in recent decades in many research laboratories. However, a broad molecular-weight distribution requires the further processing of synthesized hydrocarbons, which is similar, in principle, to oil refining. Unlike the methods of synthesis considered below, drawbacks of this process are a low efficiency of the catalysts used (from 0.05 t m^{-3} h^{-1} for the traditional process to 0.15 t m^{-3} h^{-1} for the developed improved variants) and poorly controlled selectivity.

The synthesis of methanol and competitive (to some extent) synthesis of dimethyl ether are characterized by a higher efficiency and high selectivity. Below we will consider mainly these processes and their role in the production of synthetic motor fuels.

In almost all cases, the first stage is oxidative. For natural gas, this stage is presented by different types of reforming, and gasification is the first stage for solid carbon-containing materials. The choice of syngas processing method requirements to its composition, mainly, to the H_2/CO ratio, which, in turn, affects the choice of the method for processing the initial natural gas or other raw materials. These requirements are the most rigid for the synthesis of methanol ($H_2/CO > 2$). As a result, the steam and steam-oxygen reforming of the natural gas have advantages, while syngas obtained in other processes needs enrichment in hydrogen. The DME synthesis and Fischer—Tropsch synthesis are less fastidious, so that the syngas obtained by the dry reforming of methane or by its oxidation with oxygen by coal gasification *etc.*, becomes appropriate. Let us consider the kinetics and mechanism of particular reactions.

Synthesis of methanol

The knowledge of methanol synthesis mechanism is basic for understanding the essence of several transformations shown in Scheme 1.

Presently, methanol is one of the large-scale chemicals (>30 million tons per annum). The improvement of purification methods made it possible to use the high-activity and selective copper-containing catalysts (ICI) for methanol production.

The mechanism of methanol synthesis over the copper-containing catalysts has been studied in rather detail. It was believed for a long time that methanol is formed by the hydrogenation of carbon monoxide

$$CO + 2\,H_2 \rightarrow CH_3OH. \qquad (1)$$

Later, detailed studies[3—7] revealed that the synthesis of methanol can be described by a system of exothermic reactions

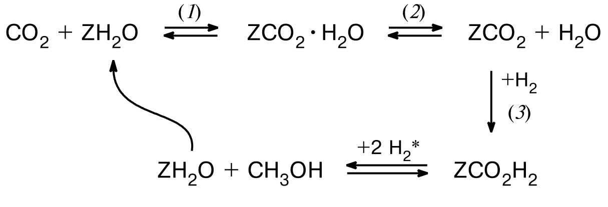
$$CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O \qquad (50.1\ \text{kJ mol}^{-1}), \qquad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (40.9\ \text{kJ mol}^{-1}). \qquad (3)$$

"Excess" oxygen atom migrates reversibly between the CO_2 and H_2O molecules. Although the stoichiometry of the final transformations can approximately be expressed by Eq. (1), the system of reactions (2) and (3) represents, in fact, a molecular chain reaction that can be initiated only by the introduction of CO_2 or H_2O. Independent proofs were obtained by different variants of the kinetic method, including tracer technique.

As a result of the studies, the detailed mechanism of methanol synthesis was established (Scheme 2).[7]

Scheme 2



* Macrostep.

Its specific features are determined by the fact that CO_2 and H_2O molecules are strongly bind to an active site of the surface, and their desorption time scales amount to hours. Since a water molecule forms in each cycle of methanol synthesis (see Scheme 2), in the framework of classical views, the synthesis of methanol should almost cease right after the first cycle. Nevertheless, the synthesis occurs successfully due to the reaction of adsorption substitution

$$ZA + B_{gas} \rightleftharpoons ZAB \rightleftharpoons ZB + A_{gas}, \qquad (4)$$

where Z is a copper-containing active site on the surface.

A similar reaction has first been proposed[8] for the system of cyclohexane dehydrogenation over platinum catalyst. Its occurrence in the catalysts of methanol synthesis (and several others) was experimentally proved in our laboratory.[7]

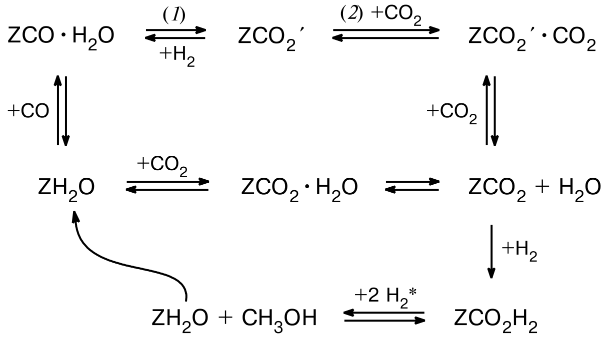
As a result of substitution (see Scheme 2, steps (*1*) and (*2*)), H_2O molecules strongly bound to the copper-containing active site are replaced by strongly bound CO_2 molecules. The characteristic time scale of the substitution reaction is shorter than that of methanol synthesis, *i.e.*, substitution occurs rather rapidly to play a role of a channel providing exchange between the gas phase and adsorbed layer. The formed ZCO_2 is likely a surface carbonate. The first step of its reduction involves hydrogen from the gas phase and is rate-determining. The formed ZCO_2H_2 (most likely, formate) is rapidly hydrogenated to methanol (with water release), so that the corresponding macrostep is close to equilibrium. A methanol molecule is released into the gas phase, and water remains on the active site, which serves as the beginning of the next cycle.

The last supplement to the mechanism was obtained[9] by studying the kinetics of methanol synthesis and simultaneously occurring the water gas shift reaction (3). It turned out that these reactions are conjugated due to an additional reaction route for transitions between ZH_2O and ZCO_2 during interactions with CO and H_2, respectively. Taking into account this conjugation, the mechanism of methanol synthesis is described by Scheme 3 in which the route with conjugation is reflected by steps (*1*) and (*2*).

Although the assignment of structures of intermediates remains unproved (based on interpretation of IR spectroscopic measurements made by independent researchers), the sequence of their transformations was established unambiguously and confirmed by an independent experiment.

The mechanistic data made it possible to create a kinetic model of the reaction, which was further confirmed experimentally and, in turn, to use this model for improving the process technology.[10] It should be mentioned that possibilities for increasing the efficiency of methanol synthesis are restricted because of an unfavorable thermodynamics of the process. However, this difficulty can be surmounted by a combination of the methanol synthesis with other reactions (see below).

Scheme 3



CO_2 and CO_2' are different forms of adsorbed CO_2.

* Macrostep.

The kinetic features of the methanol synthesis were repeatedly discussed (see Ref. 7). They are typical of reactions involving strongly bound particles.[11] In this case, in particular, a nontrivial nonlinear relation is observed between the denominator of the kinetic equation and the partial pressure of components, which either is unknown and approximated by a power or another function or is described by exotic models (involvement of different sites in the reaction, their heterogeneity, *etc.*).

The kinetic curves for methanol synthesis from gas mixtures with different concentrations of carbon oxides (in which either CO_2 or CO prevails) are presented in Fig. 1. The partially deactivated catalyst was used for which specific features of the reaction are especially pronounced, including an increase in the reaction rate with

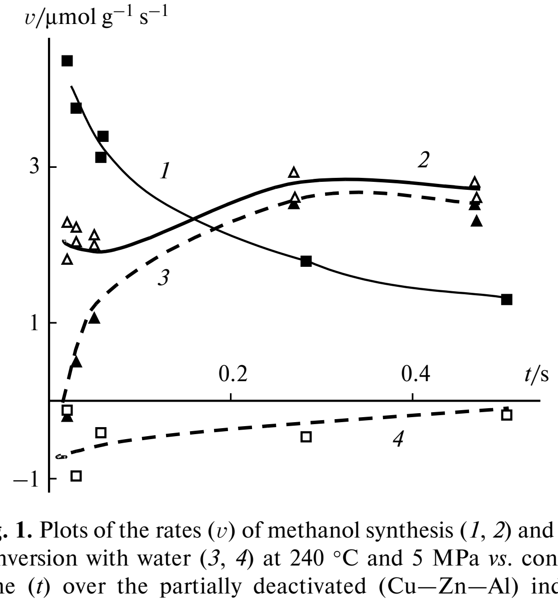


Fig. 1. Plots of the rates (v) of methanol synthesis (*1*, *2*) and CO conversion with water (*3*, *4*) at 240 °C and 5 MPa *vs.* contact time (t) over the partially deactivated (Cu—Zn—Al) industrial catalyst using the gas mixtures (vol.%): CO, 3.6; CO_2, 21.8; H_2, 74.3 (*1*, *4*) and CO, 18.3; CO_2, 3.2; H_2, 77 (*2*, *3*). Curves are calculation and points are experiment.

the contact time elongation. For both initial mixtures, experimental points coincide with calculated points, illustrating the applicability of the kinetic model based on Scheme 3.

Concluding this Section, let us consider briefly the specific features of methanol synthesis from syngas. As mentioned above, the process consists of the reactions of methanol synthesis (reaction (2)) and water gas shift reaction (3). The thermodynamic restrictions of the first reaction (methanol synthesis) cause relatively low conversions per pass and, correspondingly, a necessity of gas mixture circulation with an intermediate separation of the methanol and water that formed. The second reaction improves this situation by decreasing the water concentration directly in the reaction zone, so that a conversion of 15—20% per pass can finally be achieved in an industrial reactor.

A decrease in the water concentration is also favorable for the process from the kinetic viewpoint, because water strongly inhibits methanol synthesis.[7] Correspondingly, an efficient catalyst for methanol synthesis should also exhibit a high activity in the water gas shift reaction. In fact, in the process of methanol synthesis, the water concentration is usually close to equilibrium in this reaction and is determined, in fact, by the CO : CO_2 ratio in the initial syngas. The higher this ratio, the lower the water concentration, and the higher the efficiency of the catalyst in methanol synthesis. At the same time, CO_2 is necessary for the synthesis of methanol: its complete removal from the reaction mixture ceases the reaction. Therefore, there is an optimum concentration of CO_2 in the initial mixture, whose value is rather low (<3%), which makes it possible, in principle, to use gas mixtures with a favorable CO : CO_2 ratio of an order of 10.

In the traditional technology, only the fresh gas composition satisfies this requirement. The CO_2 content somewhat increases and that of CO decreases sharply in the circulation gas, so that the ratio of their concentrations in the gas mixture finally becomes close to unity. It follows from this that the traditional technology of methanol synthesis is not quite optimum and characterized by considerable potentialities for enhancing the catalyst efficiency. These possibilities were used in the study,[10] where a method for methanol synthesis in a cascade of flow-type units was proposed. The cascade of flow-type units is completed with a circulation unit to separate methanol and water after each reactor. The method makes it possible to enhance the efficiency of the catalyst volume unit by 1.5—2 times, thus demonstrating possibilities of increasing the efficiency of the process on the basis of studying its kinetics and mechanism.

Thus, the thermodynamic and kinetic factors restrict the efficiency of the process of methanol synthesis; these restrictions can partially be surmounted by the use of special methods: a cascade scheme, a three-phase process, *etc*. As shown below, the situation changes dramatically for the one-step DME synthesis from syngas; although the synthesis of methanol remains to be a key reaction, it is possible to avoid thermodynamic restrictions.

Dimethyl ether as new energy source

The inclusion of dimethyl ether into the number of significant energy resources was sensational.*

During a long time, researchers were not greatly interested in DME, which is reflected in its production, being presently ~150 thousand tons per year, *i.e.*, rather moderate value compared to the level of oil and gas refining. At present, DME is mainly used in the production of aerosols exploring such its properties as nontoxicity and the absence of odor, due to which DME is an ideal stuff. An interest in DME renewed in the 1980—90s, most likely, because of its possible use instead of freons (DME degrades rapidly in atmosphere). Many patents on the production of DME and intense studies of leading companies in this direction appeared in this period.

However, although ideas to use DME as an energy source were advanced (see, *e.g.*, Ref. 16), they were not developed, because DME is a gas under ambient conditions and more accessible ethanol with the same calorific value is more convenient in use. It seemed promising to use DME as a raw material for the synthesis of high-molecular ethers, which have already recommended themselves as high-octane additives to the fuel. Studies of synthesis and application of DME as a motor fuel have become intensely developed after publication of the works.[12—15]

A novel industrial potentially large-scale application is rather seldom for a known and relatively simple chemical substance. Naturally, questions appear, of which two problems are the most important: prospects or, more exactly, scales of possible use of DME as a motor fuel and possibilities to develop its large-scale production. The prediction on the first problem is fairly weak, because the solution is associated with administration decision making. Although the use of DME does not require a serious reconstruction of an engine, considerable capital investments are needed to create an infrastructure (service stations, *etc*.). Therefore, now we can evaluate market challenges only on the basis of the properties of DME as an

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* This sensational report appeared in spring 1995, when the research group of all-world recognized companies Amoco Co., Haldor Topsoe A/S, AVL Powertrain Engineering, Inc., and Navistar International Transportation Co., whose speciality is oil and gas processing, catalysis, engines, and transport, announced DME as a new ecologically safe diesel fuel at the International Congress and Exhibition in Detroit.[12—15] Subsequent approvals of independent experts resulted in the situation that after 1996 DME was mentioned in the foreign press only as "diesel fuel of the XXI century".

energy source. These properties will be considered briefly below.

Dimethyl ether as a substance and energy source

Dimethyl ether is a colorless gas or, after liquefaction, a colorless thin fluid. Some properties of DME are presented below.[14]

Parameter		Value
Molecular weight		46.07
Melting point/°C		−138.5
Boiling point/°C		−24.9
Critical temperature/°C		127
Critical pressure/bar		53.7
Vapor pressure (bar):	at 20 °C	5.1
	at 38 °C	8
Heat of vaporization/kJ kg^{-1} (at −20 °C)		410

At the pressure $p \geq 8$ atm and an appropriate temperature (≤38 °C), DME is a liquid. It is clear that difficulties typical of diesel fuel which are related to an increased viscosity at low temperatures do not appear when DME is used as liquid.

Among common energy resources, propane and butane are closest to DME by physical properties. The properties of these three substances are compared in Table 1.[15]

The data presented show that, compared to propane and butane, DME has an enhanced solubility in water (70 g are equivalent to ~36 L of gaseous DME) and 1.5-fold lower calorific value. Both are caused by the presence of an oxygen atom, composing approximately one third of the molecular weight, in the DME molecule. Other properties are close to the corresponding parameters for the compared gases, except for a wider interval of explosion concentrations, which is close to a similar interval for ethanol (3—15 vol.%).

Table 1. Some properties of DME, propane, and butane

Properties	DME	Propane	Butane
Boiling point/°C	−24.9	−42.1	−0.5
Vapor pressure (20 °C)/bar	5.1	8.4	2.1
Viscosity of liquid /cP	0.15	0.10	0.18
Density of liquid (20 °C)/g m^{-3}	668	501	610
Relative density (with respect to air)	1.59	1.52	2.01
Solubility in water/g L^{-1}	70	0.12	0.39
Calorific value/MJ kg^{-1}	28.43	46.36	45.74
Explosibility limits in air (vol.%)	3.4—17	2.1—9.4	1.9—8.4
Self-ignition temperature/°C	235	470	365

Table 2. Some properties of diesel and alternative fuels

Property	DME	DF	Methanol	Ethalol	Methane
Calorific value /MJ kg^{-1}	28.8	42.5	19.5	25.0	50.0
Density /g cm^{-3}	0.66	0.84	0.79	0.81	—
Cetane number	55—60	40—55	5	8	—
Self-ignition temperature/°C	235	250	450	420	650
Air to fuel ratio	9.0	14.6	6.5	9.0	17.2
Boiling point/°C	−25	180—370	65	78	−162
Evaporation heat (20 °C) /kJ kg^{-1}	410	250	1110	904	—
Explosibility limits (% in air)	3.4—18	0.6—6.5	5.5—26	3.5—15	5—15

A comparison of the properties of DME, traditional diesel fuel (DF), and alternative fuels, such as methanol, ethanol, and methane,[17] (Table 2) suggests that DME, as a fuel for a diesel or compression engine, surpasses rival fuels, including the traditional fuel. Its only drawback is a decreased (compared to those of DF and methane) calorific value, which is partially compensated by better economy of an engine[13,17] and the absence of expenses (including power expenses) for exhaust neutralization.

A combination of the high cetane number and low boiling point provides a good "cold start" of an engine; however, the main advantage of DME as a motor fuel is, undoubtedly, the exhaust purity along with a remarkable decrease in noise. The exhaust contains no soot, and the content of CO and NO_x decreases sharply compared to that for a diesel engine operating on the traditional fuel (see Refs. 12—17). The exhaust of an engine working on DME corresponds to the requirements of international standards without neutralization.

It should be noted in conclusion that a possibility of using DME as an energy source in gas power stations and other plants instead of natural gas, *etc.* is widely discussed in addition to its use as a diesel fuel. The subsequent, mostly engineering problem is a possibility of fast development of DME production and its cost for large-scale production.

Synthesis of dimethyl ether

The traditional route of dimethyl ether synthesis is the dehydration of methanol.

$$2\,CH_3OH = CH_3OCH_3 + H_2O \qquad (23.4\ \text{kJ mol}^{-1}) \qquad (5)$$

This reaction occurs easily over almost any dehydrating catalyst, for example, γ-Al_2O_3, at relatively low temperatures (250—300 °C). However, a more efficient process is the direct synthesis of DME from syngas. Since the temperatures of methanol synthesis and its dehydration are close, both processes can be carried out in the same reactor and, moreover, over the same bifunctional catalyst. Even a mechanical mixture of the catalysts for methanol synthesis and dehydration can be used for this purpose. In this case, the following exothermic reactions occur simultaneously:

$$CO_2 + 3\,H_2 = CH_3OH + H_2O, \qquad (2)$$

$$CO + H_2O = CO_2 + H_2, \qquad (3)$$

$$2\,CH_3OH = CH_3OCH_3 + H_2O. \qquad (5)$$

This combination of reactions is exclusively favorable. Indeed, both products of the thermodynamically restricted reaction of methanol synthesis are removed from the reaction zone to convert in reactions (3) (water) and (5) (methanol). As a result, the direct synthesis of dimethyl ether from syngas turns out to be much more efficient than the two-step process (methanol synthesis followed by its dehydration). Some parameters of the direct DME synthesis over the developed copper-containing catalysts[19] are presented in Table 3 in comparison with the synthesis of methanol.

As can be seen, the direct DME synthesis provides much higher conversions per pass conversion and efficiency of the catalyst than those for methanol synthesis. It should be emphasized that the efficiency values are related to the bulk of catalyst in which the "methanol component" composes only some part, so that differences in parameters for methanol synthesis under the conditions of DMA synthesis would be more substantial.

Differences in technical parameters affect the process economy. According to estimation in Ref. 20, the cost of DME in the one-step synthesis from syngas is by 5—10% lower than that of an equivalent amount of methanol. Close values of the difference in cost (~20%) calculated to an energy capacity unit of the product are presented.[21] In other words, DME produced in the one-step synthesis is cheaper than the raw materials for its production by the traditional two-step synthesis.

Table 3. Comparative parameters of the synthesis of methanol and direct synthesis of DME

Reaction	*p*/MPa	Efficiency*	Conversion "per pass" (%)
Synthesis of metanol (catalyst 51-2, ICI)	8	0.4	10—15
Synthesis of DME (catalyst IPS RAS)	10	0.6—1.6	60—89

* t(t of catalyst)$^{-1}$ h^{-1}.

In our laboratory, we have investigated the kinetics of DME synthesis with a maximally possible reliability. For this purpose, an information on mechanisms of all reactions that occur in the framework of the process obtained in independent studies was used. Based on these data, we developed the kinetic models of the reactions. The corresponding scheme of reactions involved in the methanol synthesis and CO conversion with water was discussed above. To describe methanol dehydration, we used a scheme[11] similar to Scheme 2, taking into account specific features related to the strong adsorption of components of the reaction mixture on active sites. This scheme agrees with the structural scheme proposed previously.[22] The model consistent with experiment theoretical kinetic for methanol dehydration has been obtained[23] (Fig. 2).

A combination of this model with the kinetic model for methanol synthesis made it possible to describe the kinetics of the overall process of the direct DME synthesis from syngas. Success of this findings seemed doubtful, because the mutual influence of the reactions and new properties of the medium could change (and for some catalysts, change in fact) the properties of active sites of the surface. Nevertheless, in this case, the model obtained agrees satisfactorily with experiment (Fig. 3).

In conclusion, let us list some specific features of the process developed for the direct DME synthesis from the syngas.[19]

1. Favorable thermodynamics; for a good engineering solution, the conversion "per pass" exceeds 50%.

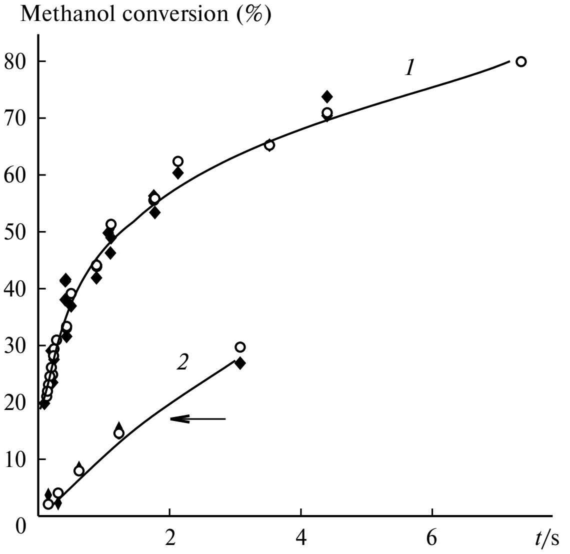

Fig. 2. Kinetics of methanol dehydration over the catalyst γ-Al_2O_3 (light points are calculation by the theoretical kinetic model, and dark points are experiment): *1*, CH_3OH (0.5—1 atm); *2*, H_2O (0.5 atm)—CH_3OH (0.5 atm).

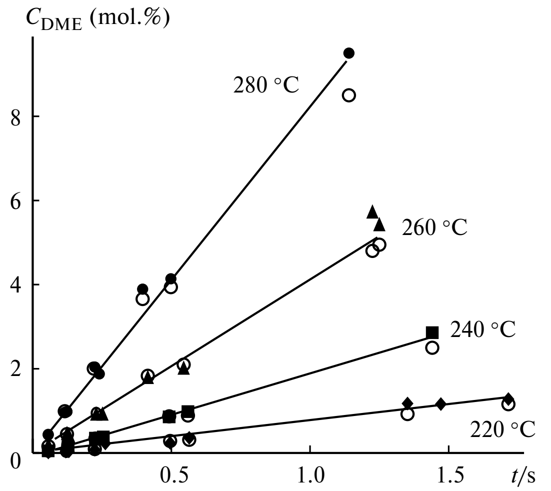

Fig. 3. Kinetics of direct DME synthesis from syngas over the catalyst developed at the IPS of the RAS (light points are calculation by the theoretical kinetic model, and dark points are experiment).

2. Considerable heat evolution; therefore, reactors with a efficient heat removal are needed to perform the process.

3. Process is indiscriminate in feedstock: it utilizes the syngas of arbitrary composition, including that from dry reforming of natural gas, gasification of coal and/or plant residues, methane oxidation with air, *etc.*

4. Stoichiometry of the overall process is determined by the composition of syngas and conditions. The limiting stoichiometric equations are $2\,CO + 4\,H_2 = CH_3OCH_3 + H_2O$ for excess hydrogen in syngas and $3\,CO + 3\,H_2 = CH_3OCH_3 + CO_2$ at hydrogen deficiency.

5. High selectivity: only methanol, CO_2, and H_2O are by-products.

Due to these features, the synthesis of DME is especially attractive for processing the carbon-containing feedstock to produce motor fuels.

Synthesis of dimethyl ether in a scheme of processing of carbon-containing feedstock to hydrocarbon motor fuel

The existing and expected methods for processing of carbon-containing feedstock to liquid hydrocarbon motor fuel can be summarized by a simple scheme

Natural gas, coal,
oil or plant feedstock →
→ syngas → methanol → hydrocarbons. (4.1)

In the framework of this scheme, dimethyl ether is a nonisolable intermediate in the step of methanol conversion to hydrocarbons. It was *a priori* doubtless that hydrocarbons can be obtained directly from DME and, correspondingly, the step of methanol synthesis can be replaced by the direct synthesis of DME from syngas.

Then the scheme of the overall process takes the form

Natural gas, coal,
oil or plant feedstock →
→ syngas → DME → hydrocarbons. (4.2)

It follows from the above-discussed features of the direct DME synthesis from syngas that the second step (DME synthesis) is much more efficient than the methanol synthesis (see Table 3). However, it is of interest to clear up the effect of this replacement on the other steps.

We have studied* DME conversion to gasoline on laboratory high-pressure pilot plants. The modified zeolite** and other catalysts*** were used. It was shown that DME is readily converted into hydrocarbons at 300—400 °C. We also synthesized gasoline directly from a reaction mixture coming from the reactor of DME synthesis, *i.e.*, gasoline was obtained from syngas in two successively arranged reactors (as well as in one reactor). The DME formed in the first reactor converts to hydrocarbons in ~100% yield. The resulting gasoline is characterized by high qualitative parameters: the absence of sulfur (by definition), a low content of unsaturated hydrocarbons (~1 wt.%) and benzene (tenths and hundredths percentage), and a moderate content of aromatic hydrocarbons (to 30 wt.%). In this case, the octane number of gasoline was found to be about 92 (by the research method). It is also significant that the products of synthesis contained hydrocarbons only up to C_{12}.

Based on the above-mentioned feedstock-indiscriminate character of DME synthesis, we attempted to prepare DME from syngas of different compositions, including a "poor" syngas containing below 40 vol.% of raw materials (gas mixture from methane oxidation with air) and a gas mixture with the ratio $H_2 : CO = 1 : 1$ that imitates the products of solid feedstock gasification. In all the cases, the resulting DME was almost completely converted to hydrocarbons.

The whole process of natural gas processing to gasoline was carried out on a pilot plant**** in a series of short-term runs. A basically new process of methane oxidation with air in a high-temperature reactor, which was created[24] on the basis of rocket technologies, was used as the first stage. The results obtained confirmed the data of laboratory pilot plants. A unique feature of this plant is

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* Cooperative study with the Laboratory headed by E. V. Slivinskii (Institute of Petrochemical Synthesis RAS).

** The catalyst was produced at the Laboratory headed by E .S. Mortikov (Institute of Organic Chemistry, RAS).

*** Prepared in our laboratory.

**** The process was carried out on a pilot plat at the Primorskii Scientific Technical Center of the Rocket Space Corporation "Energiya" [24] in cooperation with the Baltic State Technical University, the Institute of Petrochemical Synthesis of the RAS, and the Institute of Organic Chemistry of the RAS.

not only the use of new technologies but also the fact that all stages of natural gas processing occur under the same pressure (~5 MPa) without additional compression.

Thus, the third step in the scheme (4.2) and its combination with step (2) can easily be performed for almost any composition of syngas, which is, in fact, a substantiation of the modified scheme (4.2) for natural gas (carbon-containing raw materials) processing to motor fuels.[25]

The inclusion of the direct DME synthesis into the processing system can exert the greatest effect on the choice and conditions of performing the stage of syngas production. Since syngas of almost any composition is appropriate for the synthesis of DME, the synthesis of fuels can use the products of gasification of various solid carbon-containing materials, whose application would be inappropriate or too expensive for the production of syngas with a "methanol synthesis" composition.

Among other processes, high-temperature methane oxidation is a convenient method for syngas production. The most economic variant of oxidation gives syngas with the ratio $H_2 : CO = 1.6$, and this composition should be corrected to produce methanol. For DME synthesis, this syngas can immediately be fed to processing. Even a poor syngas obtained by methane oxidation with air is appropriate for the synthesis of DME and, correspondingly, gasoline. The aforementioned pilot plant worked with namely such a gas. The syngas produced by dry methane reforming is appropriate for the direct DME synthesis. In future, it seems most important to involve the products of coal gasification and renewable organic raw materials into the production of motor fuels, although their purification is expensive.

In any case, taking into account new possibilities for using the modified scheme of processing (4.2), we believe that in the nearest future synthetic fuels will be competitive in the market of motor fuels. Thus, the one-step DME synthesis from syngas is a key stage of processing of various carbon-containing feedstock into motor fuels.

Storage and transportation of hydrogen as motor fuel

In long-term outlook, we can expect that hydrogen would appear as an environmentally safe motor fuel,[26] which is associated, however, with a necessity to solve several problems. The most important of them are, most likely, the production of hydrogen (including especially pure hydrogen for fuel cells) and its storage and transportation.

The methods for hydrogen production are well developed in industry. These are, first of all, steam reforming of methane producing a molecule the most rich in hydrogen

$$CH_4 + 2\,H_2O = CO_2 + 4\,H_2. \qquad (6)$$

However, 44 g of CO_2 are formed per each 8 g of the produced hydrogen even in an idealized variant of complete conversion and 100% selectivity. In other processes of hydrocarbon (or, more widely, organic) raw materials refining, this ratio is lower. It is most likely that the single environmentally pure route of hydrogen production is electrolysis of water

$$2\,H_2O = 2\,H_2 + O_2. \qquad (7)$$

In this case, the consumed energy returns by hydrogen burning with inevitable losses, because the outputs of both processes are lower than 100%. In other words, the use of a hydrogen engine in an environmentally safe vehicle is one of the methods for utilizing an electric energy with conversion to mechanical work. Let power engineering specialists judge about profits of this direction. Still, not only hydrogen production, but also the methods of storage and transportation of hydrogen are left in the chemistry domain.

The use of metal hydrides for this purpose is restrained so far by instability of the latter in multiple absorption—desorption cycles. Nevertheless, one can use substances from which hydrogen can be obtained by simple chemical reactions accessible aboard a vehicle. These reactions can be the dehydrogenation of hydrocarbons and steam reforming of hydrogen-containing compounds. Both reactions occur at appropriate temperatures (300—400 °C) and, in addition, are endothermic, *i.e.*, make it possible to utilize a portion of heat from the exhaust. They differ substantially in hydrogen "capacity" of raw materials.

Cyclohexane is the richest in the released hydrogen, and its dehydrogenation to benzene occurs rather easily

$$C_6H_{12} = C_6H_6 + 3\,H_2. \qquad (8)$$

Let us compare the output of hydrogen in this reaction with that in the steam reforming of methanol or dimethyl ether.

$$CH_3OH + H_2O = CO_2 + 3\,H_2 \qquad (9)$$

$$CH_3OCH_3 + 3\,H_2O = 2\,CO_2 + 6\,H_2 \qquad (10)$$

In reaction (8), 84 g of the raw material (cyclohexane) is needed to obtain 6 g of hydrogen. The same result will be obtained in reaction (9) by the conversion of methanol (32 g) and water (18 g), while in reaction (10) 46 g of DME + 54 g of water (totally, 100 g) give 12 g of hydrogen. The advantage of steam reforming is evident. In the light of the aforesaid, an objection arises concerning the formation of CO_2 in reactions (9) and (10). However, taking into account that both synthesis of methanol and DME can involve CO_2 utilization,[27] we can reject this argument.

The steam methanol reforming occurs rather selectively over copper-containing catalysts. However, ~1% CO is formed as a by-product, being a poison for fuel cells. An admissible content of CO for using in different variants of fuel elements ranges from 10 to 100 ppm. Therefore, to obtain pure hydrogen appropriate for using in fuel elements, one should combine the steam reforming of methanol and/or DME with hydrogen purification from CO to this admissible content. If these problems were solved successfully, methanol (or DME) can be used as a convenient carrier for storage and transportation of hydrogen.

Therefore, in our laboratory we studied the methanol steam reforming[28] and purification of produced hydrogen from CO traces by the catalytic oxidation of the latter.[29,30] The studies are in progress now, meanwhile some preliminary results can be presented.

Methanol steam reforming

The results of studying methanol steam reforming, including the reaction kinetics, are widely presented in recent publications. However, even the authors of the most comprehensive (in our opinion) work[31] use an empirical method to select a kinetic model, which usually allows one to describe an experiment only within the studied region of conditions.

The purpose of our study is to obtain a theoretical kinetic model for the reaction on the basis of its mechanism. Methanol steam reforming (reaction (9)) was studied in flow-type reactors over the copper-containing catalysts at different water to methanol ratios (1.3 : 1 mixture was used as a basis) in a pressure interval of 0.1—2.1 MPa. The reforming itself over the copper-containing catalysts can be accompanied by the reverse water gas shift reaction (reduction of CO_2 to CO)

$$CO_2 + H_2 = CO + H_2O, \tag{-3}$$

and the formation of methyl formate followed by its decomposition to a $CO + H_2$ mixture.[32]

$$\begin{array}{c} 2\,CH_3OH = CH_3OCHO + 2\,H_2 \\ \downarrow \\ 2\,CO + 2\,H_2 \end{array} \tag{11}$$

At temperatures above 200 °C, this reaction usually occurs until complete decomposition of methyl formate.

Reactions (−3) and (11) produce a CO admixture in hydrogen. Therefore, at the first stage of the study, we estimated the role of these reactions in the overall process.

Under the conditions of methanol steam reforming, the water gas shift reaction at 250—300 °C is close to equilibrium, and reaction (11) is almost completely suppressed in the presence of water in the gas phase. The contribution of reaction (11) becomes remarkable only at high methanol concentrations (partial pressure ~10 atm, 300 °C). This is caused by differences in bond strengths of molecules of the components in the reaction mixture with active sites described by the series $CO < CO_2 < CH_3OH < H_2O$ and by the intense occurrence of adsorption substitution reactions discussed above.

At high H_2O concentrations, almost all active sites are covered with the adsorbed water or the products of its transformations, *i.e.*, the initial state of an active site in reforming corresponds, in the framework of designations accepted above, to a state ZH_2O. The same state is final in Schemes 2 and 3 of methanol synthesis. According to the principle of microscopic reversibility, all steps in these schemes take place for the reverse reaction, so that the mechanism of steam reforming can be presented by Schemes 2 and 3 written in an inverse direction. Correspondingly, a theoretical kinetic model for the reaction of steam methanol reforming can be constructed.

A comparison of the experimental kinetic data for methanol steam reforming over the copper-containing catalyst with the calculated data obtained from this model shows satisfactory agreement between calculation and experiment (Fig. 4). Moreover, both the methanol synthesis and its steam reforming can be described by the same equation with the same values of parameters. This procedure was based on the data of the study[33] of the methanol synthesis and steam reforming (according to the terminology of the authors, "hydrolysis").

The results of calculation of the kinetics of methanol steam reforming with the same parameters as those in the kinetics of its synthesis agree with the experimental data (Fig. 5). This means that, despite a vastly different composition of the reaction mixture, the nature of active sites and their properties remain the same in both the synthesis and steam reforming of methanol.

The efficiency of the copper-containing catalyst in the steam reforming of methanol obtained in the study ex-

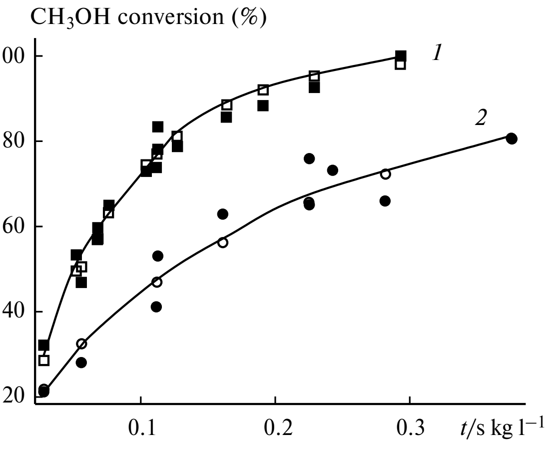

Fig. 4. Kinetics of methanol steam reforming over the copper-containing catalyst: initial water—methanol mixture (1.3 : 1) (light points are calculation by the theoretical kinetic model, and dark points are experiment), 308 °C; 6 atm (*1*) and 21 atm (*2*).

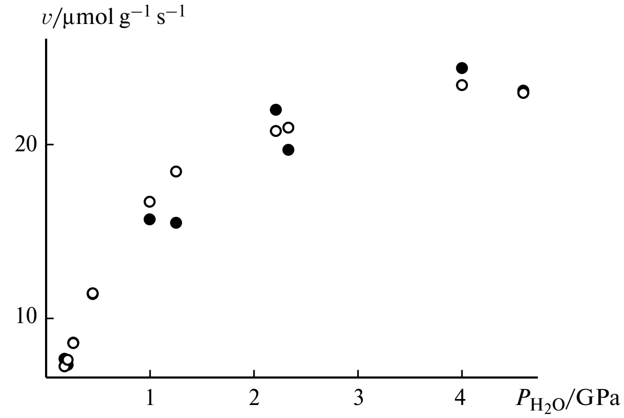

Fig. 5. Calculation of the kinetics of methanol steam reforming under atmospheric pressure according to the published data.[33]

ceeds 10 L (L of catalyst h)$^{-1}$ with a satisfactory selectivity, which makes it possible to use rather small devices for methanol processing. For instance, ~1 L of the catalyst is required to process a methanol equivalent corresponding (by energy content) to a gasoline consumption of ~10 L h^{-1}.

CO oxidation in the presence of excess hydrogen

The oxidation of CO in the presence of hydrogen (selective CO oxidation) is under intense study in the recent time due to the problem of hydrogen purification for fuel cells (see, *e.g.*, Refs. 34 and 35). However, conclusions about the mechanism and kinetics of the reaction are diverse and contradictory. Nevertheless, it can be established reliably that the selectivity of oxygen consumption (fraction of reacted oxygen consumed in CO oxidation) decreases with the temperature increase.

Many researchers observed a fast increase in CO conversion with temperature. This phenomenon is often determined by the term "ignition." It should be noted that ignition cannot occur, as a rule, in heterogeneous catalysis because of intense heterogeneous chain termination. However, a spontaneous transition of the reaction to the outer-diffusion region (Frank-Kamenetskii named this process "ignition of catalyst surface")[36] can be observed. In the case when a positive thermal flux q^+, caused by an exothermic reaction, becomes equal to a negative thermal flux q^-, related to heat removal, in combination with the condition $\mathrm{d}q^+/\mathrm{d}T > \mathrm{d}q^-/\mathrm{d}T$, the jumpwise transition of the reaction to the outer-diffusion region occurs with the temperature increase and is accompanied by a spontaneous temperature increase in the catalyst bed. It follows from this that, varying heat removal conditions, the same reaction can be carried out in the regime of surface ignition or in a standard regime without ignition.

Taking into account this specific feature, we studied the selective CO oxidation in excess hydrogen over the Pt-containing catalyst in flow-type reactors under absolutely different heat removal conditions.[30]

Reactor 1 (with a high rate of heat removal) was almost isothermal. The reaction was carried out in a metallic cylindrical reactor with a coaxially located metallic tube. A catalyst loading was diluted with an inert material in a ratio of 1 : 10, and the resulting mixture was placed in a circular gap between the tube and reactor walls.

Quartz cylindrical reactor 2 (with a low rate of heat removal) was close to adiabatic, so that the temperature of a gas mixture increased with its movement along the reactor axis. A catalyst loading was placed in the reactor without dilution with an inert material. The temperature of the gas mixture was measured at the inlet and near the outlet of the catalyst bed with an error of ±0.1° (thermocouples in a thin metallic case in the catalyst bed). The temperature of the furnace was specified by a special programmer.

A residual content of CO in a dried gas mixture was monitored using a BINOS 100 IR analyzer (error <1 ppm). To simulate mixtures obtained by methanol steam reforming, the reaction was carried out in the presence of CO_2 and water vapor.

It was shown that in reactor 1 CO oxidizes in the kinetic region. In reactor 2 at a low temperature, the reaction occurs in the kinetic region, and the temperature in the catalyst bed increases simultaneously with an increase in the temperature of the furnace until the critical temperature of catalyst surface ignition is achieved. When the critical temperature is achieved, the temperature in the catalyst bed increases spontaneously at an unchanged temperature of the furnace with a simultaneous decrease in the residual content of CO. After the regime of surface ignition was established, a change in the temperature of the furnace has a weak effect on the temperature of the gas in the catalyst bed and residual content of CO in the gas mixture until (with a temperature decrease) the critical temperature of surface attenuation would be achieved. After this critical value is achieved, the temperature in the catalyst bed changes jumpwise and the CO content increases, so that both parameters change to the level that was observed before ignition. A hysteresis characteristic of the phenomenon of surface ignition is observed.

The apparent activation energy was determined by two methods: from the dependence of the critical ignition temperature on the flow rate of the gas flux (see Ref. 37b) and using the traditional method for data obtained in an isothermal reactor. Both values virtually coincided (13 and 14 kcal mol^{-1}).

It seems that the most important of the results obtained is that the residual CO content, in all cases under optimum conditions, was much lower in the regime of surface ignition than that in an isothermal reactor where the reaction occurred in the kinetic region.

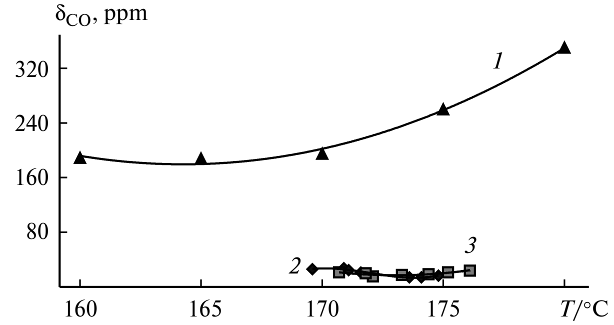

Fig. 6. Plots of the residual content of CO (δ_{CO}) *vs.* temperature of the gas in an isothermal reactor (*1*) and at the outlet of the catalyst bed in reactor 2 (*2*, *3*). Composition of the starting mixture (vol.%): CO, 0.85; O_2, 0.85; CO_2, 17; H_2, 33; H_2O, 17; residue is N_2. Flow rate (h^{-1}): 13500 (*1*), 12800 (*2*), and 14200 (*3*).

The plots of the residual CO content *vs.* temperature in the isothermal reactor (curve *1*) and in the "hot point" near the outlet of the catalyst bed in reactor 2 (curves *2* and *3*)[30] are shown in Fig. 6. It is seen that the residual CO content at the same temperature and flow rate in the regime of catalyst surface ignition is by an order of magnitude lower.

Thus, the regime of catalyst surface ignition is more favorable than the isothermal regime for selective CO oxidation in excess hydrogen. This is caused by the temperature distribution over the catalyst bed, which is more favorable for selective oxidation: the reaction in the frontal part of the reactor occurs at lower temperatures and at relatively high oxygen concentrations.

The data presented already show that very low concentrations of residual CO required for hydrogen use in fuel elements become accessible under the conditions of catalyst surface ignition. In addition, 1 L of the catalyst can provide purification of more than 10000 L hydrogen per hour, including also in the presence of H_2O and CO_2 (see Fig. 6).

Conclusion

In conclusion, we would like to emphasize once more a key role of the synthesis of dimethyl ether in the considered array of processes for producing motor fuels from alternative raw materials. The most important feature of the modified scheme of processing, including the direct DMF synthesis from syngas, is the fact that the H_2 : CO ratio in the syngas is not critical. The modified scheme of processing is characterized by improved technical economical parameters and also makes it possible to use syngas of different compositions. This extends substantially both the list of potential raw materials sources and the set of methods for their processing. As a whole, the scheme provides a universal route of processing various raw materials to produce motor fuels. When taking into account, in addition, that DME itself and gasoline produced from it are energy resources of improved ecological quality, we can expect that synthetic fuels produced by this method will be competitive against the background of fuels of petroleum origin.

At the same time, the brief discussion of potentialities of using methanol (and, probably, DME) to produce hydrogen for fuel elements shows that modern catalysts and purification methods can presently provide methanol processing to pure hydrogen with an efficiency appropriate, in principle, for boarding the corresponding devices on a vehicle. The future will show what method would be chosen in practice.

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