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## CATALYSIS IN CHEMICAL AND PETROCHEMICAL INDUSTRY

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# Contemporary Trends in Methanol Processing

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**Abstract**—The current structure of the production and consumption of methanol is reviewed. The main processes of methanol processing and catalysts for their implementation are highlighted: the production of formaldehyde, hydrocarbons (MTH), olefins (MTO), and the production of hydrogen from methanol by means of steam reforming, partial oxidation, autothermal reforming, and decomposition.

**Keywords:** methanol use, methanol production volumes, catalysts, methanol processing

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## INTRODUCTION

### 1. Structure of the Current Consumption of Methanol

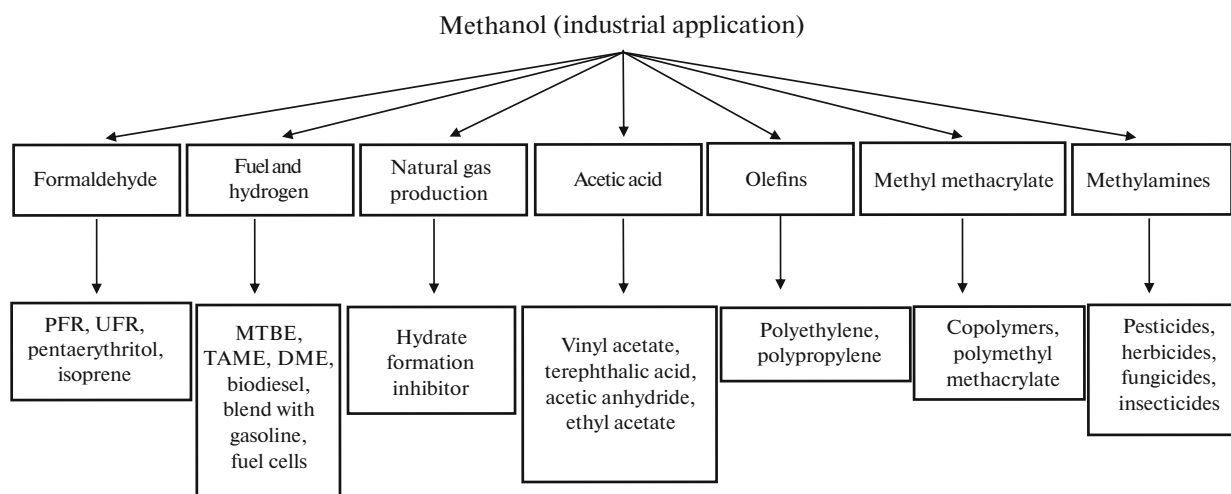
Methanol is a highly valuable chemical that has numerous uses as a fuel, an initial reagent in the synthesis of other chemicals [1–3], and a solvent. Lines of the industrial use of methanol are shown schematically in Fig. 1. It can be seen that methanol is the basis for the production of a great many chemicals with a variety of applications. Urea–formaldehyde and phenol–formaldehyde resins; paints and varnishes; heat-insulating materials; plastics; coatings; and products for protecting plants are manufactured on its basis. The production of fuel and hydrogen have in recent decades become the most important fields of methanol's application.

Around 60% of all methanol is currently produced from natural gas. The remainder is based on coal (especially in China, where more than 67% of all methanol is produced from coal) and biomass [4]. The volume of methanol produced in the world is steadily growing. Figure 2 shows a diagram based on data from [2]. As can be seen, the annual growth in methanol production can be estimated at 4–7%, except for the unfavorable year 2020. The total consumption of methanol worldwide in 2013 was 60.7 million t. Its constant growth is apparent and is projected to be 6% per year, up to 109 million t in 2023. The growth in consumption is primarily associated with China (the world's main consumer of methanol), the needs of which are expected to grow from 30 million t in 2013 to 67.5 million t in 2023. In 2016, Russia produced 3.7 million t of methanol, or approximately 5% of all global production [5].

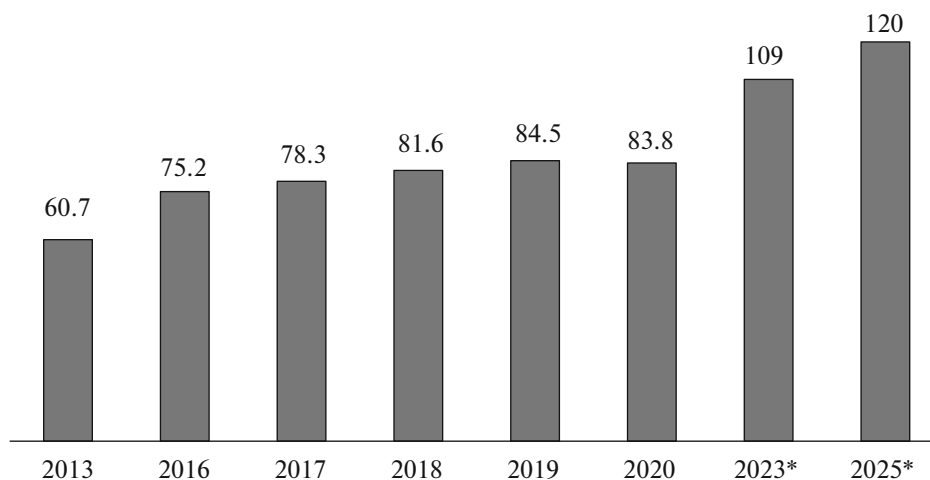
Estimates of global capacities for methanol production differ according to various sources. According to the estimate in [6], the world capacity in 2013 was 98.3 million t. It was reported in [7] that the global methanol production capacity was 148 million t in 2019, and it will be more than 310 million t by 2030. The data [2] presented in Fig. 3 show that global methanol production capacities grew by 150% between 2013 and 2021, but no more than 70% were in operation.

Driving factors behind the increase in methanol production are the expansion of its use in transportation as a fuel mixed with gasoline, and the production of hydrocarbons and olefins. The difference between the global and Russian of methanol consumption in 2019 and is illustrated in Figs. 4–6, along with the change in the structure of world methanol consumption predicted for 2025. Forty-six percent of all methanol was spent to obtain formaldehyde in Russia in 2019, while the world figure was 29%. Worldwide, up to 23% of all methanol was used for transportation. In Russia, this figure was 8%. It is predicted that the share of methanol used for the production of formaldehyde will fall to 22% worldwide by 2025, while the proportion spent on transportation will rise to 27% [2].

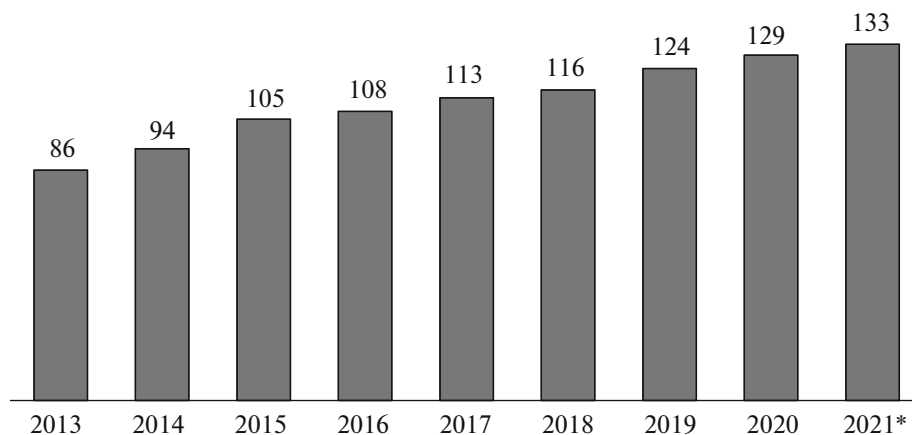
Methanol is a toxic product and has fairly low added value. Transporting it over long distances is therefore undesirable, and it is advisable to combine the production of methanol with one of the means of its secondary processing into valuable chemical products or components of motor fuels.



**Fig. 1.** Main trends in the industrial utilization of methanol. Abbreviations: MTBE, methyl*tert*-butyl ether; TAME, *tert*-amyl methyl ether; PFR, phenol–formaldehyde resin; UFR, urea–formaldehyde resin.



**Fig. 2.** World production of methanol, millions of tons [2]. Asterisks denote forecasts.



**Fig. 3.** World methanol production capacities, millions of tons [2]. Asterisks denote forecasts.

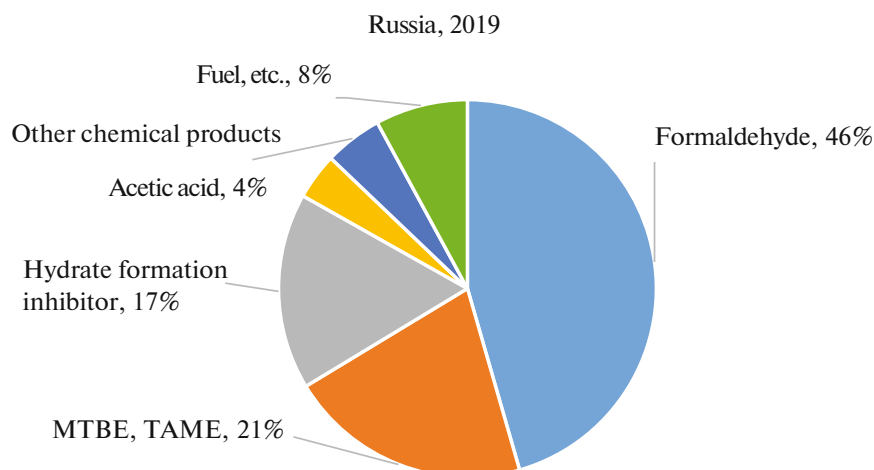


Fig. 4. Structure of methanol consumption in Russia in 2019 [2].

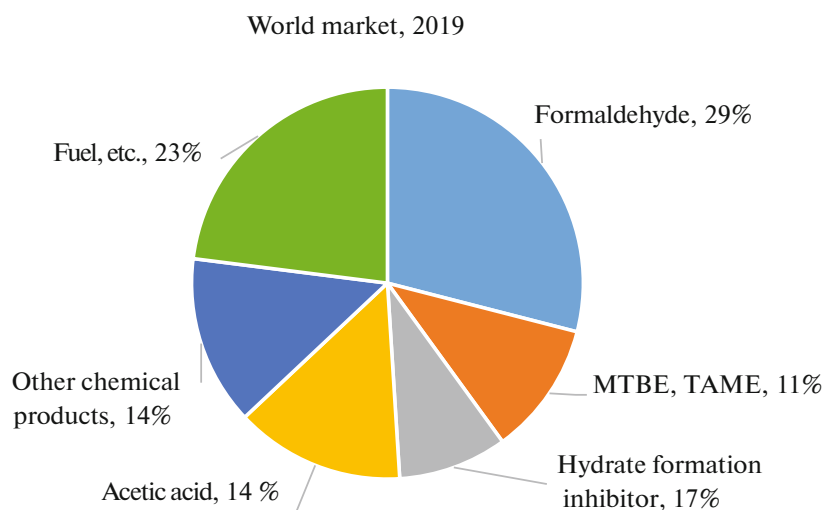


Fig. 5. Structure of methanol consumption worldwide in 2019 [2].

## 2. Oxidation of Methanol to Formaldehyde

The oxidation of methanol to formaldehyde remains the main way of processing it in Russia. Formaldehyde production is growing at an average rate of 4% per year, and IHS analysts predict this trend will continue.

Oxidation is done on Fe–Mo oxide catalysts inside tubular reactors, using pure oxygen at temperatures of 350–450°C. Rates of methanol consumption in the process are around 0.43 t per tonne of 37% formalin. Formaldehyde is mainly used for the production of phenol–formaldehyde (25%) and urea–formaldehyde resins and concentrates (35% worldwide and 60% in Russia). Production is therefore distributed between relatively small enterprises. Typical large-scale production of formaldehyde ranges from 40 to 200 thousand t per year.

The current leaders in the production of formaldehyde are Perstorp AG and Süd Chemie (now Clariant), which control around 85% of the market for catalysts of this process. When designing a gas processing complex, it is advisable to combine processes for the production of formaldehyde, urea, and urea–formaldehyde resins or concentrates.

## 3. Conversion of Methanol into Components of Motor Fuels

Increased direct use of methanol as a vehicle fuel is expected in coming years. M15 fuel (15% methanol/85% gasoline) is widely used in five provinces in China and accounts for around 8% of China's gasoline market. Since 2009, the European Union has approved the introduction of up to 3% methanol in

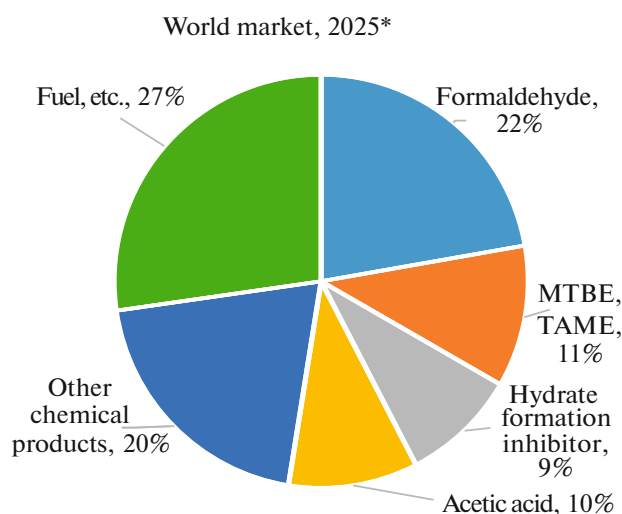


Fig. 6. Predicted structure of methanol consumption worldwide in 2025 [2].

gasoline. Options for using methanol-containing fuels have yet to be considered in Russia.

Despite the potential use of methanol as a fuel for road transport (whether direct or mixed with gasoline), modern engines would require substantial upgrades, making it unattractive for the automotive industry. Along with its low calorific value, high volatility, corrosiveness, and toxicity, methanol's ability to retain water makes its direct use problematic. It therefore makes more sense to convert methanol into mixtures of gasoline fraction hydrocarbons and use it directly, or in combination with regular gasoline.

It was discovered in 1977 that methanol could be converted into hydrocarbons [8]. The first industrial process for converting natural gas through methanol into gasoline was Mobil Oil's MTG (methanol-to-gasoline) technology, implemented at the Methanex plant in New Zealand in 1985. The plant produced 1,700 t of AI-92 gasoline per day (620,000 t/yr) with 87–89% selectivity toward gasoline in the total amount of hydrocarbons produced. The yield of gasoline was around 11 kg from 1 GJ of natural gas (i.e., around 477 t from 1 million m<sup>3</sup>). The plant operated from 1985 to 1996, after which the production of gasoline at the plant was stopped due to insufficient economic efficiency of the process.

ExxonMobil's R&D work in the following years led to the second generation of the MTG process (EMRE MTG), which was successfully implemented in China in 2009 at the Jincheng Anthracite Mining Group (JAMG) coal processing plant in Shangqi Province [9]. The plant's capacity is 2500 barrels of gasoline per day (about 105,000 t/yr). Gasoline accounts for 88.9% of the hydrocarbon products of the new MTG process.

In 2015, ExxonMobil and the Sinopec Engineering Group (SEG) agreed to jointly develop ways of con-

ducting the MTG process in a fluidized bed reactor. An MTG fluidized bed reactor would reduce operating costs and improve energy efficiency, relative to a fixed bed reactor. Judging from the protocol published in [10], it was recently decided to establish production based on this development.

Even though the above industries use coal as a feedstock for methanol production, the second generation of MTG technology could be promising for gas processing complexes.

MTG technology produces up to 1.3 t of water as a by-product per each ton of gasoline produced. Each plant for processing natural gas according to the natural gas → MeOH → MTG scheme must therefore include a unit for water purification and utilization. Another MTG by-product that requires isolation and disposal is durene (1,2,4,5-tetramethylbenzene, C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>4</sub>). This aromatic compound has a high melting point (79.7°C) and its presence in the fuel results in the formation of solid deposits in the carburetor or in the engine's injector. Traditional gasoline contains no more than 0.3% durene, while its content in MTG products is 3–6 wt %. Stages of the separation of the heavy fraction, its hydrogenation to convert durene, and the subsequent mixing of heavy and light gasoline fractions into the final product have therefore been introduced into the new version of the MTG process (EMRE MTG).

In addition to MTG technology, Haldor Topsoe offers a process for converting natural gas into gasoline. This process, called Topsoe Improved GASoline Synthesis (TIGAS) also dehydrates methanol to gasoline, but the steps for synthesizing methanol (and dimethyl ether) and converting it into gasoline are done in a single reaction cycle. The first (pilot) TIGAS technology began operation in February 2013.

The methanol-to-gasoline (MTG) process is conducted on a variety of zeolite catalysts that include SAPO-11 and H-ZSM-5. Using zeolite catalysts, methanol can be processed into a mixture of branched and aromatic hydrocarbons (53% branched alkanes, 12% branched alkenes, 7% cycloalkanes and 28% aromatics), i.e., gasoline. This synthetic gasoline contains no sulfur or nitro compounds, making it environmentally friendly. The catalytic properties of zeolite catalysts in converting methanol into hydrocarbons depend on the geometry of the pore channels of the zeolites, their specific surface area, and such acidic properties as the type, strength, number, and distribution of acid sites. Numerous studies have been performed to optimize such characteristics of a catalyst as its phase composition and porous structure, its specific surface area, and the acidic properties of its surface, along with preventing the formation of coke and extending the catalyst run time [11–14]. Studies of zeolite HZSM-5 [15] have shown that the main cause of deactivation is coke deposition. Acid, alkaline, and steam heat treatment are used to control the acidic

**Table 1.** Catalysts and MTG Process Conditions, According to Different Sources

Catalyst	Conditions	$X_{\text{MeOH}}$ , %	$S_{\text{MeOH}}$ , %	Reference
Nano-ZSM-5	370°C, 1 atm,	100	88.5	[18]
Meso-ZSM-5	WHSV = 2.6 h <sup>-1</sup>	70	57.7	
H-ZSM-5-Na <sub>2</sub> CO <sub>3</sub>	400°C, 1 atm, WHSV = 28 h <sup>-1</sup>	75	100	[19]
7% CuO-H-ZSM-5	400°C, WHSV = 28 h <sup>-1</sup>	97	42	[20]
H-ZSM-5 -0.1 M CaCO <sub>3</sub>	400°C, 1 atm,	99.7	38.7	[21]
H-ZSM-5 -0.1 M Na <sub>2</sub> CO <sub>3</sub>		99.8	38.6	
ZSM-5	350°C, 11 atm, WHSV = 1.2 h <sup>-1</sup>	100	59	[22]
ZSM-5/MCM-48	10 atm, WGSV = 2 h <sup>-1</sup>			[23]
	340°C	93.1	18.5	
	360°C	96.1	23.7	
	380°C	98.3	27.6	
	400°C	99.2	41.2	
	420°C	99.5	42.3	

properties of zeolite catalysts. The authors of [16, 17] summarized results from recent years on both optimizing the characteristics of catalysts and the effect of such process parameters as temperature, pressure, and feed space velocity and composition on the selectivity and productivity of methanol-to-gasoline conversion. Table 1 presents results from studying the catalytic properties of ZSM-5 zeolites, both modified and as parts of composites. Data from different authors differ considerably, but we may generally conclude that in order to increase the selectivity toward hydrocarbons of the gasoline fraction and suppress deactivation, the temperature of the process should be no more than 400–420°C, and the optimum pressure is at least 10 atm.

Active research continues on reactors and processes for converting methanol into gasoline. It was shown in [24] that the traditional two-stage process is most effective in the synthesis of hydrocarbons. The typical composition of products is liquid hydrocarbons C<sub>6</sub>–C<sub>8</sub>, 23%; gaseous C<sub>1</sub>–C<sub>5</sub>, 65%, and heavy C<sub>9</sub>–C<sub>12</sub>—10%.

The possibility of using dimethyl ether as diesel fuel was discussed in the late 1990s. Dimethyl ether can be obtained quite easily by dehydrating methanol on acid catalysts. Even though transitioning to this fuel would require the modification of engines, such a program was seriously considered both in Russia and around the world. However, extensive studies performed by leading vehicle manufacturers showed that dimethyl ether is not an effective lubricant, and using this fuel in its pure form results in rapid wear of an engine's piston rings. Today, dimethyl ether is used only as a component of motor fuel in mixtures with liquefied petroleum gas (the propane–butane fraction, or PBF) that are 20–25% of the latter. DME is also used as a sol-

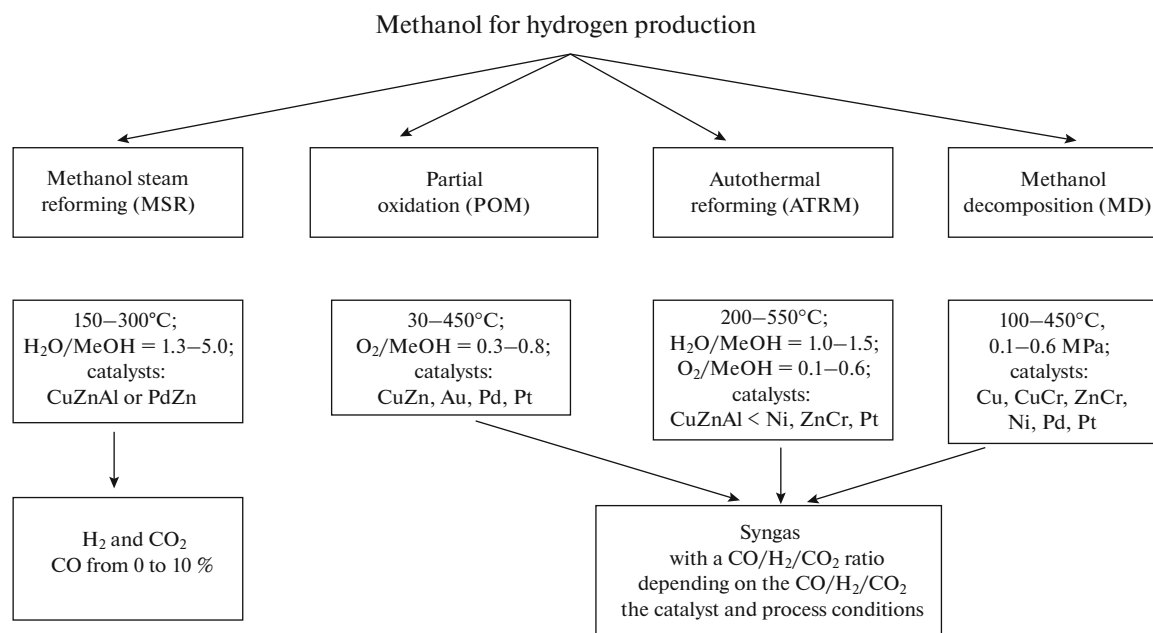
vent, refrigerant (in pure form and in mixtures), and as a raw material in the production of acetic acid.

#### 4. Methyl Tert-Butyl Ether

Methyl tert-butyl ether is an additive that raises the octane number of a fuel. It is produced via the methylation of isobutylene. Despite the effectiveness of this additive and its low toxicity (4th class of hazard), it is still environmentally unfriendly due to its high (unlimited) solubility in water and extreme resistance to biodegradation (there are no microorganisms in nature that decompose this substance). Because of this and strong suspicions of its carcinogenicity [25], California (in 2003), New York (in 2004), and 25 other US states either banned the use of MTBE completely or limited its content in gasoline to 0.5–1%. In Europe, the content of MTBE is limited to 5% (it is typically 1–1.6%). In Russia, the formal limit is 15%, considerably more than the normally introduced 5–12%. The production of MTBE within the gas processing complex is limited by a lack of isobutylene and can be considered only an additional means when choosing the main process for the conversion of methanol to olefins, in which isobutylene is a by-product. Russian analysts [26] report that the MTBE market in Russia has declined since 2014, due to reduced production of high-octane gasoline at some refineries. Demand is also influenced by factories transitioning to the consumption of components of their own production.

#### 5. Hydrogen Production

Recent decades have seen growing worldwide interest in methanol as a carrier of liquid hydrogen capable of producing high-purity hydrogen when necessary. The main ways of processing methanol into hydrogen are shown schematically in Fig. 7. These are



**Fig. 7.** Processes for the synthesis of hydrogen from methanol via the reactions of steam reforming (MSR), partial oxidation (POM), autothermal reforming (ATRM), and the decomposition of methanol.

steam reforming [27–32], partial oxidation [33–36], autothermal reforming [30, 37, 38], and methanol decomposition [39–41].

The authors of [42] discussed and compared the current main ways of producing hydrogen from methanol. Particular attention was given to the development of catalysts and technologies. Catalysts containing copper are highly active and selective, but extremely sensitive to poisons and have low stability. Attempts to use other metals and oxides (e.g., zinc, zirconia, oxides of cerium, chromium, and other transition metals) are being examined. Spinel-structured catalysts are highly active and more stable. Pd-Zn alloy catalysts also have high selectivity toward  $H_2$  and  $CO_2$ . Microreactors are thought to be promising [43]. New forms of structured catalysts have been proposed (e.g., porous copper fiber felts). Monolithic designs provide maximum surface area for coverage with catalytically active components and lower drops in pressure. Membrane reactors can greatly improve the productivity of hydrogen.

### 6. Methanol to Olefins (MTO and MTP)

MTO and MTP are two related processes developed only in recent decades. MTO from UOP/Hydro [44] and MTP from Lurgi [45] compare favorably to the composition of products from traditional petrochemical cracking processes that result in high yields of light olefins ethylene and propylene (Fig. 8). The conversion of methanol to olefins (MTO) is therefore one of the most preferred ways of synthesizing olefins. The proceeds at atmospheric pressure on such acid

catalysts as HZSM-5 or SAPO in the 350–450°C range of temperatures. According to [46], the selectivity toward ethylene and propylene on SAPO-34 catalysts at UOP plants is 85–100%. The commercial production of olefins from methanol began in 2010 [47–49].

At best, MTO catalyst should combine a high concentration of acid sites of moderate strength and a special structure of micropores and mesopores. Intensive research continues around the world to improve MTO catalysts and increase their selectivity and (most importantly) stability under the conditions of reactions [50].

It is proposed that the problem of increasing the lifetime of MTO catalyst be solved by creating a special mesoporous composite structure based on SAPO-5 and SAPO-34 microporous zeolites. The authors of [51] claimed that such a composite catalyst has a longer lifetime and better selectivity toward light olefins than microporous zeolite.

MTO allows us to obtain mainly propylene and ethylene, and the ratio of the two can be adjusted in the wide range of 1 to 1.8 during operation, depending on the needs of the stages of polymerization. Additional MTO products are butylenes and higher molecular weight products. They can total as much as 0.3 t per each ton of ethylene produced, but this figure can be reduced by using the UOP/OCP olefin cracking process developed by UOP. This process was successfully tested in a pilot plant in Feluy (Belgium) in 2010 and is used industrially today at factories built using UOP technology (Fig. 9). Cracking allows us to reduce

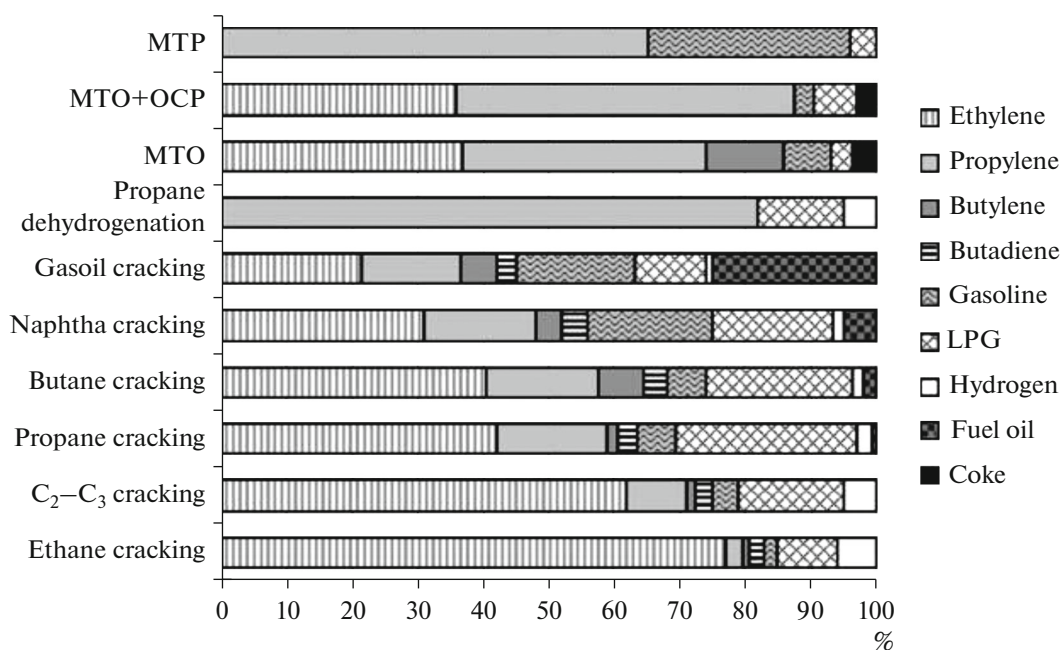


Fig. 8. Comparison of the composition of MTO, MTP, and traditional petrochemical cracking products [49].

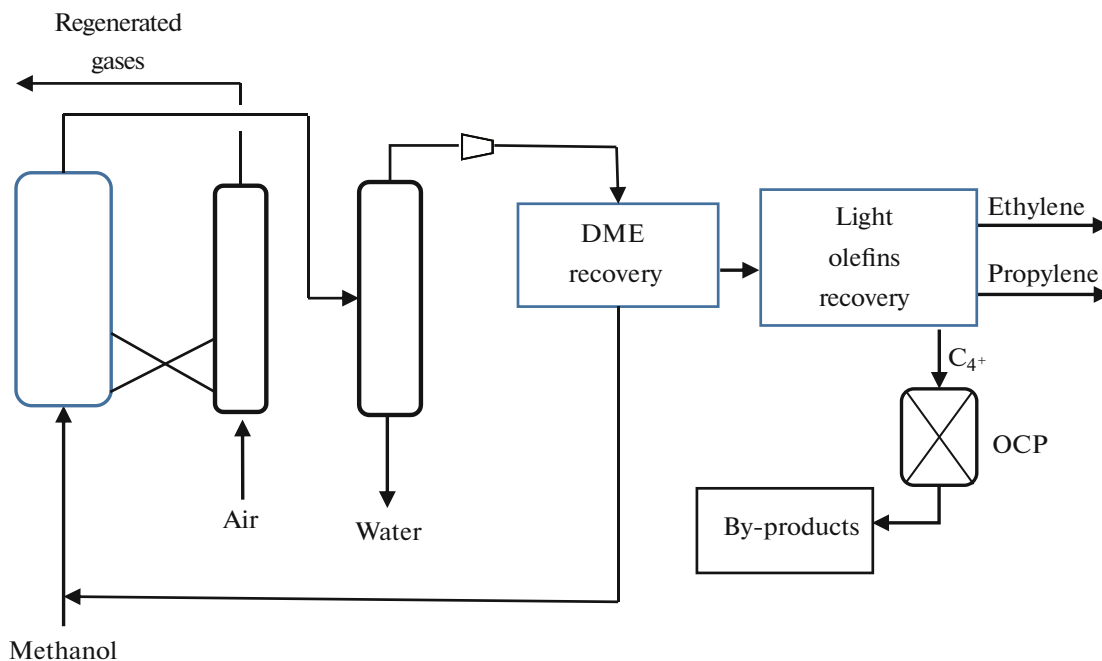


Fig. 9. Scheme of the advanced MTO process with the cracking of OSP higher olefins [49].

the rates of methanol consumption from 3 t to 2.6 t per each ton of olefins.

An alternative way of using butylenes that is promising under the conditions of Russia is the production of MTBE.

The MTP process mainly produces propylene of a purity suitable for polymerization. By-products (gasoline and a small amount of the propane–butane fraction (PBF)) are commercial. The resulting gasoline meets Russian standards, and its composition differs from the traditional one in a much larger proportion of

the branched olefin fraction. Perhaps this is why Lurgi experts recommend it as a component of motor gasoline when mixed with traditional gasoline. According to Lurgi, methanol + MTP synthesis, which consumes 12.3 million m<sup>3</sup> of synthesis gas per day (corresponding to a consumption of approximately 4.7 million m<sup>3</sup> of natural gas per day or 1.7 billion m<sup>3</sup> of natural gas per year) and yields around 1.7 million t/yr of intermediate methanol (Lurgi MegaMethanol, which is similar to Lurgi Atlas), would allow us to obtain 470 000 t of propylene per year and 143 000 t of gasoline per year as the final product.

China is now an internationally recognized leader in both catalyst and MTO process technology. In the 2010s, the Dalian Institute of Chemical Physics (Dalian, China) developed a process similar to UOP MTO technology: DMTO. Its modification with olefin cracking is referred to as DMTO-II. This process is used today in several coal processing plants in China. In 2011, Sinopec launched a plant using its own MTO technology. By the end of 2019, 14 DMTO and DMTO-II plants with a total capacity of 7.670 million t/yr were launched and are operating in China [52]. A detailed study of the composition, means of preparation, mechanisms of the formation of promising SAPO-34 catalyst [53–59], and the mechanism of the reaction [60] gave Chinese specialists the opportunity to develop and launch a new, highly efficient DMTO-III process. This process uses a highly efficient reactor with a fluidized bed of catalyst that raises the productivity of olefins from 600 thousand to 1 million t/yr and reduces the consumption of methanol from 2.97 to 2.64 t per each ton of olefins [61].

Both MTO and MTP technologies produce water as a by-product. The amount of water produced is around 55 wt % of the processed methanol or 1.2 t per each ton of products (olefins and hydrocarbons) produced. In the version of the Lurgi MTP plant described above, the production of water will total 936 000 t/yr. The structure of a natural gas processing plant using MTO/MTP technology must therefore include a water purification and utilization unit.

In addition to those operating in China, at least seven plants under construction or operating with a total capacity of around 3 million t/yr now process methanol into olefin monomers ethylene and propylene. Among these are Rio Polymeros (Brazil), a plant for the production of ethylene (520 000 t/yr), and Qatofin (Qatar), which produces ethylene and polyethylene (450 000 t/yr).

The selectivity of the process toward the formation of olefins remains a problem, due to the short life of the catalysts. Ones based on Si-Al-P zeolites SAPO-34 have proven to be the best commercial catalysts for MTO. The key factors determining the yield of olefins are the tendency to form coke, the size of the crystals, and the strength of the acid sites of the catalysts. The process parameters also greatly affect a catalyst's life

and selectivity. The higher the temperature, the lower the selectivity toward olefins, due to the more active formation of coke. The authors of [62] highlighted the main factors responsible for the deactivation of MTO catalysts, giving particular attention to SAPO-34 catalysts.

Diluting methanol with water favorably affects the selectivity and lifetime of catalysts. It increases the yield of olefins, while reducing the formation of coke, DME, and aromatic hydrocarbons [63–65].

The estimate of capital costs given in [66] shows they are approximately equal for MTP and MTO technologies. Preference for one of the two technologies thus depends solely on the forecast of the market for olefins and polyolefins.

### 7. Carbonylation of Methanol to Acetic Acid

The Monsanto and Cativa processes are conducted at pressures of 30–60 atm and temperatures of 150–200°C on iodide–carbonyl complex anions of rhodium (Monsanto) or iridium and ruthenium (Cativa) [67]. The mechanism of the process includes six homogeneous stages with the intermediate formation of methyl iodide, its carbonylation on the iodide–carbonyl complex of the metal to acetyl iodide and hydrolysis of the latter to acetic acid. HI is present in the reactor as a reaction promoter. The design of the reactor is simple and the standard for a homogeneous process reactor with forced stirring using an electric stirrer. Both processes have exceptional selectivity (99%), but the resulting mass still requires two to three stages of distillation to isolate the product and remove impurities of propionic acid (0.12–0.2% in the Monsanto process) and organic iodides. The Monsanto and Cativa processes are similar and can be used on the same production line with very few changes.

The Monsanto process was the first to be developed (1966). Today, however, it has been virtually superseded by the Cativa process, due to the much lower cost of iridium and ruthenium, relative to rhodium.

Acetic acid is the initial material in a huge tree of different processes for producing acetates, including butyl acetate, vinyl acetate and derivatives of it, cellulose acetate, and terephthalic acid.

### 8. Methanol-to-Aromatics (MTA)

Such aromatic hydrocarbons as BTX (benzene, toluene, and xylenes) are popular organic reagents that until recently were obtained in the naphtha reforming process. Due to the depletion of oil reserves, ways of producing aromatic hydrocarbons based on the conversion of methanol are now being developed around the world [68]. MTA is usually done on modified zeolite catalysts of the HZSM-5 type at elevated pressures and temperatures of around 450°C [69]. It has been



shown that including transition metals in zeolites is an effective way of controlling the direction of the methanol conversion reaction toward the formation of aromatic compounds [69–71]. Of the many possible combinations of zeolites and transition metals, ZSM-5 displayed the most promising characteristics for converting methanol to hydrocarbons, and Zn is one of the metals with the greatest ability to activate aromatic compounds [72, 73]. In such a bifunctional catalytic system, the Brønsted and Lewis acid sites of the zeolite catalyze the conversion of methanol to aromatic hydrocarbons. The selectivity of methanol conversion into aromatic compounds is also influenced by its porous structure [74]. The formation of aromatic hydrocarbons is mainly due to the restriction of diffusion along the hierarchical ZSM-5. The lowest BTX selectivity is obtained over mesoporous ZSM-5 with supported SiO<sub>2</sub>, due to its weaker acidity and the clogging of pore orifices. The deactivation of ZSM-5 catalysts has been attributed to the formation of insoluble coke. It has also been shown that the formation of mesopores and silylation of their outer surfaces inhibit the deactivation of catalysts.

There are methanol processing processes that require specific reagents, so in this review we shall not discuss methyl halides, methyl methacrylate, or dimethyl terephthalate. Methylamines are toxic and corrosive substances used in different organic syntheses, so it is better to obtain them directly at the site of their subsequent use, and they are therefore also excluded from this review.

## CONCLUSIONS

Except for the oxidation of methanol to formaldehyde, all of the processes described above for processing methanol and catalysts for their use were developed by foreign companies. At the same time, it is obvious that the processes of processing natural gas and analogs of it into valuable chemical products are a key factor in ensuring the sustainable development and economic security of Russia. Russian industrial enterprises currently process around 43 billion cubic meters of valuable chemical products from natural gas, which accounts for 9% of its total consumption in Russia [75].

Natural gas is mainly processed to produce methanol. Further, methanol is used in the production of urea, formaldehyde, urea-formaldehyde resins and other products. However, many promising processes that are successfully used in world practice, such as the production of olefins from methanol (MTO-MTP), the conversion of methanol to arenes (gasoline) in Russia have not yet received industrial distribution. Using these processes, the volume of natural gas processed into chemical products could grow to more than 60 billion cubic meters per year just to meet the demand of the domestic market.

Since the economically effective lifetime of catalysts for most processes is 0.5 to 3 years, gas-chemical production in Russia and consumers of its products (agricultural, woodworking enterprises, the chemical industry) depend heavily on foreign supplies of catalysts produced mainly in the developed countries of Europe and the United States. The development of catalyst production technologies is therefore a prerequisite for Russia's economic security. In coming decades, Russia will be faced with the task of widely introducing technologies for the chemical processing of natural gas into valuable products and developing its own technological base as well, especially in producing catalysts for these processes.

## LIST OF ABBREVIATIONS

MTG	methanol-to-gasoline
MTO	methanol-to-olefines
MTP	methanol-to-propylene
DME	dimethyl ether
MSR	steam reforming of methanol
POM	partial oxidation of methanol
ATRM	autothermal reforming of methanol
MTBE	methyl- <i>tert</i> -butyl ether
TAME	<i>tert</i> -amyl methyl ether
PFR	phenol-formaldehyde resin
UFR	urea-formaldehyde resin
PBF	propane-butane fraction
MTA	methanol to aromatics
BTX	benzene, toluene, and xylenes

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## REFERENCES

1. Methanol Institute Official Website. [www.methanol.org/applications/](http://www.methanol.org/applications/). Cited May 25, 2021.
2. *Rynok metanola: tekushchaya situatsiya i perspektivy* (Market of Methanol: State-of-the-Art and Prospects) [https://assets.ey.com/content/dam/ey-sites/ey-com/ru\\_ru/topics/industrial-products/ey-methanol-market-overview-october-2020-rus.pdf?download](https://assets.ey.com/content/dam/ey-sites/ey-com/ru_ru/topics/industrial-products/ey-methanol-market-overview-october-2020-rus.pdf?download). Cited May 25, 2021.
3. Shapovalova, A., *Kratkii obzor rossiiskogo rynka metanola po itogam 2019 goda* (Brief Review of the Russian Market of Methanol by the End of 2019). [https://www.refinitiv.ru/blog/marketinsights/kratkij-obzor-rossijskogo-rynka-metanola-po-itogam-2019/#\\_ftn1](https://www.refinitiv.ru/blog/marketinsights/kratkij-obzor-rossijskogo-rynka-metanola-po-itogam-2019/#_ftn1). Cited May 25, 2021.

4. Roode-Gutzmer, Q.I., Kaiser, D., and Bertau, M., *ChemBioEng Rev.*, 2019, vol. 6, no. 6, pp. 209–236. <https://doi.org/10.1002/cben.201900012>
5. Vyatkin, Yu.L., Lishchiner, I.I., Sinitsyn, S.A., and Kuz'min, A.M., *Neftegaz*, 2020, vol. 4, pp. 114–118.
6. Boulamanti, A. and Moya, J.A., *Renewable Sustainable Energy Rev.*, 2017, vol. 68, part 2, pp. 1205–1212. <https://doi.org/10.1016/j.rser.2016.02.021>
7. Garside, M., Production capacity of methanol worldwide from 2018 to 2030. [www.statista.com/statistics/1065891/global-methanol-production-capacity/](http://www.statista.com/statistics/1065891/global-methanol-production-capacity/). Cited May 25, 2021.
8. Yarulina, I., Chowdhury, A.D., Meirer, F., Weckhuyesen, B.M., and Gascon, J., *Nat. Catal.*, 2018, vol. 398, pp. 398–411. <https://doi.org/10.1038/s41929-018-0078-5>
9. Hindman, M., MTG Technology. An alternative to liquid fuel production. Paper presented at the World CTL Conference, Beijing, China, 2010. <https://ru.scribd.com/document/139367979/Conference-2011-1204-MTG-World-CTL>
10. SINOPEC Engineering Official Website. Voluntary announcement: Entering into a contract for Huizhou chemical complex project (phase I) with ExxonMobil. <https://www1.hkexnews.hk/listedco/listconews/sehk/2021/0412/2021041200065.pdf>. Cited May 25, 2021.
11. Zhang, L., Wang, S., Shi, D., Qin, Z., Wang, P., Wang, G., Li, J., Dong, M., Fan, W., and Wang, J., *Catal. Sci. Technol.*, 2020, vol. 10, pp. 1835–1847. <https://doi.org/10.1039/c9cy02419k>
12. Sousa, Z.S.B., Luna, A.S., Zotin, F.M.Z., and Henriques, C.A., *Chem. Eng. Commun.*, 2020. <https://doi.org/10.1080/00986445.2021.1884552>
13. Stepacheva, A.A., Doluda, V.Yu., Lakina, N.V., Molchanov, V.P., Sidorov, A.I., Matveeva, V.G., Sulman, M.G., and Sulman, E.M., *React. Kinet. Mech. Catal.*, 2018, vol. 124, pp. 807–822. <https://doi.org/10.1007/s11144-018-1359-3>
14. Park, S., Sato, G., Osuga, R., Wang, Y., Kubota, Y., Kondo, J.N., Gies, H., Tatsumi, T., and Yokoi, T., *Chem. Ing. Tech.*, vol. 93, no. 6, pp. 1–12. <https://doi.org/10.1002/cite.202000174>
15. Pérez-Urriarte, P., Ateka, A., Gayubo, A.G., Cordero-Lanzac, T., Aguayo, A.T., and Bilbao, J., *Chem. Eng. J.*, 2017, vol. 311, pp. 367–377. <https://doi.org/10.1016/j.cej.2016.11.104>
16. Kianfar, E., Hajimirzaee, S., Mousaviand, S., and Mehr, A.S., *Microchem. J.*, 2020, vol. 156. <https://doi.org/10.1016/j.microc.2020.104822>
17. Ali, S.S. and Zaidi, H.A., *Energy Fuels*, 2020, vol. 34, no. 11, pp. 13225–13246. <https://doi.org/10.1021/acs.energyfuels.0c02373>
18. Rownaghi, A.A. and Hedlund, J., *Ind. Eng. Chem. Res.*, 2011, vol. 50, no. 21, pp. 11872–11878. <https://doi.org/10.1021/ie201549j>
19. Fathi, S., Sohrabi, M., and Falamaki, C., *Fuel*, 2014, vol. 116, pp. 529–537. <https://doi.org/10.1016/j.fuel.2013.08.036>
20. Zaidi, H.A. and Pant, K.K., *Can. J. Chem. Eng.*, 2005, vol. 83, pp. 970–977.
21. Kianfar, E., Salimi, M., Pirouzfard, V., and Koohestani, B., *Int. J. Chem. React. Eng.*, 2018, vol. 16, no. 7, pp. 1–7.
22. Wan, Z., Wu, W., Chen, W., Yang, H., and Zhang, D., *Ind. Eng. Chem. Res.*, 2014, vol. 53, no. 50, pp. 19471–19478. <https://doi.org/10.1021/ie5036308>
23. Di, Z., Yang, C., Jiao, X., Li, J., Wu, J., and Zhang, D., *Fuel*, 2013, vol. 104, pp. 878–881. <https://doi.org/10.1016/j.fuel.2012.09.079>
24. Doluda, V.Yu., Stepacheva, A.A., Lakina, N.V., Manaenkov, O.V., Molchanov, V.P., Demidenko, G.N., Matveeva, V.G., Panfilov, V.I., Sulman, M.G., and Sulman, E.M., *Int. J. Sustainable Energy*, 2018, vol. 37, no. 10, pp. 970–977. <https://doi.org/10.1080/14786451.2017.1402770>
25. Burns, K.M. and Melnick, R.L., *Int. J. Occup. Environ. Health*, 2012, vol. 18, no. 1, pp. 66–68. <https://doi.org/10.1179/107735212X13293200778947>
26. RUPEC Information and Analytical Center. <http://rupec.ru/news/43423/>. Cited May 25, 2021.
27. Yong, S.T., Ooi, C.W., Chai, S.P., and Wu, X.S., *Int. J. Hydrogen Energy*, 2013, vol. 38, pp. 9541–9552. <https://doi.org/10.1016/j.ijhydene.2013.03.023>
28. Sa, S., Silva, H., Brandao, L., Sousa, J.M., and Mendes, A., *Appl. Catal., B*, 2010, vol. 99, nos. 1–2, pp. 43–57. <https://doi.org/10.1016/j.apcatb.2010.06.015>
29. Shishido, T., Yamamoto, Y., Morioka, H., Takaki, K., and Takehira, K., *Appl. Catal., A*, 2004, vol. 263, pp. 249–253
30. Chen, W.H., and Syu, Y.J., *Int. J. Hydrogen Energy*, 2011, vol. 36, pp. 3397–3408. <https://doi.org/10.1016/j.ijhydene.2010.12.055>
31. Peppley, B.A., Amphlett, J.C., Kearns, L.M., and Mann, R.F., *Appl. Catal., A*, 1999, vol. 179, pp. 31–49.
32. Liu, X., Toyir, J., Ramírez de la Piscina, P., and Homs, N., *Int. J. Hydrogen Energy*, 2017, vol. 42, no. 19, pp. 13704–13711. <https://doi.org/10.1016/j.ijhydene.2016.12.133>
33. Agrell, J., Germani, G., Jars, S.G., and Boutonnet, M., *Appl. Catal., A*, 2003, vol. 242, pp. 233–245.
34. Agrell, J., Hasselbo, K., Jansson, K., Jaras, S.G., and Boutonnet, M., *Appl. Catal., A*, 2001, vol. 211, pp. 239–250.
35. Chen, W.H. and Guo, Y.Z., *Fuel*, 2018, vol. 222, pp. 599–609. <https://doi.org/10.1016/j.fuel.2018.03.004>
36. Chen, W.S., Chang, F.W., Roselin, L.S., Ou, T.C., and Lai, S.C., *J. Mol. Catal. Chem.*, 2010, vol. 318, pp. 36–43. <https://doi.org/10.1016/j.molcata.2009.11.005>
37. Jampa, S., Jamieson, A.M., Chaisuwan, T., Luengnaruemitchai, A., and Wongkasemjit, S., *Int. J. Hydrogen Energy*, 2017, vol. 42, pp. 15073–15084. <https://doi.org/10.1016/j.ijhydene.2017.05.022>
38. Chen, W.H. and Lin, B.J., *Int. J. Hydrogen Energy*, 2013, vol. 38, no. 24, pp. 9973–9983. <https://doi.org/10.1016/j.ijhydene.2013.05.111>
39. Liu, Y., Hayakawa, T., Ishii, T., Kumagai, M., Yasuda, H., and Suzuki, K., *Appl. Catal., A*, 2001, vol. 210, pp. 301–314.
40. Matsumura, Y. and Tode, N., *Phys. Chem. Chem. Phys.*, 2001, vol. 3, pp. 1284–1288.

41. Li, G., Gu, C., Zhu, W., Wang, X., Yuan, X., and Cui, Z., *J. Cleaner Prod.*, 2018, vol. 183, pp. 415–423. <https://doi.org/10.1016/j.jclepro.2018.02.088>
42. Garcia, G., Arriola, E., Chen, W.-H., and De Luna, M.D., *Energy*, 2021, vol. 217. <https://doi.org/10.1016/j.energy.2020.119384>
43. Gribovskiy, A.G., Makarshin, L.L., Andreev, D.V., Klenov, O.P., and Parmon, V.N., *Chem. Eng. J.*, 2015, vol. 273, pp. 130–137. <https://doi.org/10.1016/j.cej.2015.03.036>
44. Chen, J.Q., Bozzano, A., Glover, B., Fuglerud, T., and Kvisle, S., *Catal. Today*, 2005, vol. 106, nos. 1–4, pp. 103–107. <https://doi.org/10.1016/j.cattod.2005.07.178>
45. Air Liquide E&C. Lurgi MTP™ Methanol-to-Propylene. Industrial Production of Propylene. <https://www.engineeringairliquide.com/ru/lurgi-mtp-propileniz-metanola>. Cited May 25, 2021.
46. Gogate, M.R., *Pet. Sci. Technol.*, 2019, vol. 37, no. 5, pp. 559–565. <https://doi.org/10.1080/10916466.2018.1555589>
47. Tian, P., Wei, Y., Ye, M., and Liu, Z., *ACS Catal.*, 2015, vol. 5, pp. 1922–1938. <https://doi.org/10.1021/acscatal.5b00007>
48. Zhou, J., Gao, M., Zhang, J., Liu, W., Zhang, T., Li, H., Xu, Z., Ye, M., and Liu, Z., *Nat. Commun.*, 2021, pp. 12–17. <https://doi.org/10.1038/s41467-020-20193-1>
49. Kempf, R., Paper presented at the Middle East Chemical Week Conference, 2011, Abu Dhabi, UAE.
50. Kianfar, E., *Pet. Chem.*, 2021. <https://doi.org/10.1134/S0965544121050030>
51. Bal, Y., Zeng, Q., Sun, J., Song, Q., Tang, L., Zhang, W., and Liu, Z., *J. Porous Mater.*, 2021. <http://doi.org/10.1007/s10934-021-01078-0>
52. Ye, M., Tian, P., and Liu, Z., *Engineering*, 2021, vol. 7, pp. 17–21. <https://doi.org/10.1016/j.eng.2020.12.001>
53. Liu, G., Tian, P., Li, J., Zhang, D., Zhou, F., and Liu, Z., *Microporous Mesoporous Mater.*, 2008, vol. 111, pp. 143–149. <https://doi.org/10.1016/j.micromeso.2007.07.023>
54. Liu, G., Tian, P., Zhang, Y., Li, J., Xu, L., Meng, S., and Liu, Z., *Mesoporous Mater.*, 2008, vol. 114, pp. 143–149. <https://doi.org/10.1016/j.micromeso.2008.01.030>
55. Gao, S., Liu, Z., Xu, S., Zheng, A., Wu, P., Li, B., Yuan, X., Wei, Y., and Liu, Z., *J. Catal.*, 2019, vol. 377, pp. 51–62. <https://doi.org/10.1016/j.jcat.2019.07.010>
56. Wang, C., Yang, M., Tian, P., Xu, S., Yang, Y., Wang, D., Yuan, Y., and Liu, Z., *J. Mater. Chem. A*, 2015, vol. 3, pp. 5608–5616. <https://doi.org/10.1039/c4ta06124a>
57. Qiao, Y., Yang, M., Gao, B., Wang, L., Tian, P., Xu, S., and Liu, Z., *Chem. Commun.*, 2016, vol. 52, pp. 5718–5721. <https://doi.org/10.1039/c5cc10070d>
58. Wu, P., Yang, M., Zhang, W., Xu, S., Guo, P., Tian, P., and Liu, Z., *Chem. Commun.*, 2017, vol. 53, pp. 4985–4988. <https://doi.org/10.1039/c7cc01834g>
59. Wu, P., Yang, M., Sun, L., Zeng, S., Xu, S., Tian, P., and Liu, Z., *Chem. Commun.*, 2018, vol. 54, pp. 11160–11163. <https://doi.org/10.1039/c8cc05871g>
60. Wu, X., Xu, S., Wei, Y., Zhang, W., Huang, J., Xu, S., He, Y., Lin, S., Sun, T., and Liu, Z., *ACS Catal.*, 2018, vol. 8, no. 8, pp. 7356–7361. <https://doi.org/10.1021/acscatal.8b02385>
61. Wei, Y., Tian, P., Ye, M., and Liu, Z., Paper presented online at the Sino-Russian High-Level International Symposium on Catalysis, 2021.
62. Ahmad, M.S., Cheng, C.K., Bhuyar, P., Atabani, A.E., Pugazhendhi, A., Lan Chic, N.T., Witoon, T., Lim, J.W., and Juan, J.C., *Fuel*, 2021, vol. 283. <https://doi.org/10.1016/j.fuel.2020.118851>
63. Froment, G., Dehertog, W., and Marchi, A., *Catalysis*, 1992, vol. 9, no. 1, pp. 1–64.
64. Dehertog, W. and Froment, G., *Appl. Catal.*, 1991, vol. 71, no. 1, pp. 153–65.
65. Wu, X. and Anthony, R., *Appl. Catal., A*, 2001, vol. 218, nos. 1–2, pp. 241–250.
66. Vora, B., Funk, G., and Bozzano, A., in *Handbook of Petroleum Processing*, Treese, S.A., Pujadó, P.R., and Jones, D.S.J. Eds., Cham: Springer, 2015, pp. 883–904. [https://doi.org/10.1007/978-3-319-14529-7\\_14](https://doi.org/10.1007/978-3-319-14529-7_14)
67. Jones, H.T., *Platinum Met. Rev.*, 2000, vol. 44, no. 3, pp. 94–105.
68. Bender, M., Paper presented at the DGMK-Conference “New Technologies and Alternative Feedstocks in Petrochemistry and Refining”, Dresden, Germany, 2013.
69. Conte, M., Lopez-Sanchez, J.A., He, Q., Morgan, D.J., Ryabenkova, Y., Bartley, J.K., Carley, A.F., Taylor, S.H., Kiely, C.J., Khalid, K., and Hutchings, G.J., *Catal. Sci. Technol.*, 2012, vol. 2, pp. 105–112. <https://doi.org/10.1039/c1cy00299f>
70. Zhang, J., Qian, W., Kong, C., and Wei, F., *ACS Catal.*, 2015, vol. 5, pp. 2982–2988. <https://doi.org/10.1021/acscatal.5b00192>
71. Pinilla-Herrero, I., Borfecchia, E., Holzinger, J., Mentzel, U.V., Joensen, F., Lomachenko, K.A., Bordiga, S., Lamberti, C., Berlier, G., Olsbye, U., Svelle, S., Skibsted, J., and Beato, P., *J. Catal.*, 2018, vol. 362, pp. 146–163. <https://doi.org/10.1016/j.jcat.2018.03.032>
72. Shoinkhorova, T., Cordero-Lanzac, T., Ramirez, A., Chung, S.-H., Dokania, A., Ruiz-Martinez, J., and Gascon, J., *ACS Catal.*, 2021, vol. 11, no. 6, pp. 3602–3613. <https://doi.org/10.1021/acscatal.0c05133>
73. Pinilla-Herrero, I., Borfecchia, E., Cordero-Lanzac, T., Mentzel, U.V., Joensen, F., Lomachenko, K.A., Bordiga, S., Olsbye, U., Beato, P., and Svelle, S., *J. Catal.*, 2021, vol. 394, pp. 416–428. <https://doi.org/10.1016/j.jcat.2020.10.02>
74. Wang, Y., An, H., Ma, H., Zhang, X., Kang, G., and Cao, J., *Adv. Powder Technol.*, 2021. <https://doi.org/10.1016/j.apt.2021.03.037>
75. Gazprom Official Website. Russian Market of Gas. <https://www.gazprom.ru/about/marketing/russia/>. Cited May 21, 2021.