
CATALYSIS IN CHEMICAL AND PETROCHEMICAL INDUSTRY

Catalysts for Synthesizing Liquid Hydrocarbons from Methanol and Dimethyl Ether: A Review

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Abstract—Different ways of increasing the selectivity of catalysts are described for converting oxygenate to liquid hydrocarbons. Analysis of reports suggests that the main factors affecting the selectivity of zeolite-containing catalysts are the structural type and acidic properties of the zeolites. It is shown that the strength and distribution of acid sites depend on the structural type and chemical composition of the zeolite framework, and on the chemical nature of the exchange cations. Different ways of changing the acidic properties of zeolites are discussed, e.g., modifying them with cations of various elements and subjecting them to postsynthesis acidic, alkaline, and steam heat treatment.

Keywords: catalysts, zeolites, shape selectivity, acidic properties, dimethyl ether, methanol, conversion, liquid hydrocarbons, selectivity

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INTRODUCTION

The conversion of methanol (MeOH) and/or dimethyl ether (DME) into hydrocarbons (HCs) is a rapidly developing industrial process based on using an alternative carbon-containing feedstock via an intermediate stage of conversion into synthesis gas (CO–H₂ mixture) [1–9]. Most of the motor fuels now produced are of petroleum origin [10, 11]. At the same time, gasoline produced from methanol and/or DME using synthesis gas has high octane characteristics. The quality of this product compares favorably to that of gasoline synthesized from crude oil by conventional means, since the former contains no harmful impurities (e.g., sulfur and nitrogen compounds) [12].

The first works on converting MeOH into liquid HCs date back to the 1970s [13–15], when researchers at the Mobil Oil Corporation sought new ways of producing high-octane gasoline via the co-conversion of MeOH and isobutane in the presence of ZSM-5 zeolite developed by the company's employees.

The development of a single-stage procedure for DME production has stimulated great interest among researchers in the technology for synthesizing gasoline from DME produced using synthesis gas in a single stage [16–28]. This technology is promising, due to its favorable thermodynamic characteristics [25, 26]. In addition, DME is characterized by higher activity than MeOH upon conversion into liquid HCs, and less coking of the catalyst [16, 29–31].

Analysis of the main results from investigations on synthesizing liquid HCs from MeOH and DME showed that catalysts based on zeolites (largely those of the ZSM-5 type) are the ones most effective for this process. The high capabilities characteristic of zeolites allow targeted changes in their physicochemical and catalytic properties. Nonzeolitic catalysts (ZnCl₂, P₂O₅, Al₂O₃, WO₃, heteropolyacids) used in this reaction showed a rapid loss of activity, due to the coking or poisoning of active sites.

This review summarizes data presented in the current scientific literature, mostly on the effect of the structural type and acidic properties of zeolites on the activity and selectivity of zeolite catalysts for the conversion of MeOH and DME. Factors responsible for the acidic properties of zeolites (e.g., their topological features and postsynthesis treatment, the chemical composition of the zeolite framework, and the nature of exchange cations) are discussed.

EFFECT OF THE TYPE OF ZEOLITE STRUCTURE ON CATALYTIC CHARACTERISTICS

Methanol-to-gasoline (MTG) catalysts are based on zeolite ZSM-5 (Zeolite Socony Mobil-5, MFI structural type) [16, 20, 32–35]. The absence of molecules containing more than ten carbon atoms in the reaction products is attributed to the unique pore structure of the zeolite.

[†] Deceased.

The main structural unit of ZSM-5 zeolites is a 5-membered oxygen ring (these zeolites are therefore referred to as pentasil); the ring is mostly composed of SiO_4 tetrahedra, since the content of Al in the framework is low. The combination of these tetrahedra into a three-dimensional framework in crystals leads to the formation of a system of through channels of two types—straight and sinusoidal—with sizes of 5.1×5.5 and 5.3×5.6 Å, respectively, that intersect at right angles [36]. According to data on HC adsorption [37–39], the movement of molecules inside the crystals is governed by a system of pores: in catalytic processes, reactant molecules of a certain size diffuse into the crystals through channels of one type, while molecules of products of different sizes exit the zeolite through channels of the other type.

The intersections of the channels provide enough volume for ring-forming reactions and intermolecular hydrogen transfer, during which a mixture of alkenes can be converted to alkanes and aromatic HCs [34].

High-silica zeolite of the ZSM-11 type is similar to ZSM-5 zeolites in having a two-dimensional porous structure of straight 5.3×5.5 Å channels composed of 10-membered rings and intersecting at right angles [40]. ZSM-11 zeolites exhibit the same activity in the conversion of MeON into HCs as that of ZSM-5, but the former is inferior to the latter in shape selectivity [41–43]: the liquid product obtained with a selectivity of 41% is no more than 29% aromatic compounds, mostly C_9 – C_{10} (durol, 20%). When ZSM-5 is used, the dominant aromatic HCs are xylenes (C_8 products). This difference between catalytic properties is due to the different volumes of cavities formed during the intersection of pores in these types of zeolites.

Table 1 shows the structural characteristics and catalytic properties of different structural types of H^+ -form zeolites in the conversion of DME and MeOH.

Since the high octane number of gasoline synthesized via MTG in the presence of zeolites ZSM-5 is attributed to the high content of aromatic HCs, alternative zeolite catalysts must provide high contents of branched-chain aliphatic compounds in order to preserve the octane characteristics of the resulting gasoline. Macroporous MOR zeolites (12-membered channels of 6.5×7.0 Å, interconnected in one direction by 8-membered channels of 2.6×5.7 Å) and Y zeolites (12-membered channels of 7.4×7.7 Å, connecting large cavities) were studied for the production of liquid HCs from methanol [44–48]. However, test results revealed the rapid deactivation and low activity and selectivity of these zeolites when converting MeOH into liquid HCs.

In the opinion of the authors of [49], the structure of beta (BEA) zeolite (a three-dimensional porous system of intersecting channels of 5.5×5.6 and 7.1×7.6 Å; see Table 1) has features in common with the structure of both zeolite ZSM-5 (a three-dimensional porous system of intersecting channels of 5.1×5.5

5.3×5.6 Å, and a high Si : Al ratio) and zeolite Y (a system of 12-membered rings of 7.4×7.7 Å). These features can positively affect the catalytic characteristics of the zeolite in converting methanol into HCs [50–52]. However, studies show that zeolite BEA exhibits high initial activity of 83% in MeOH conversion, but it falls to 10% after 30 h on stream, with the HC yield dropping from 80 to 5%. The main products are C_2 – C_4 HCs (30–40%). The liquid products are 54.8% aromatics that consist mostly of polyaromatic compounds [53, 54] and penta- and hexamethylbenzenes [52].

Since zeolites with two- and three-dimensional porous systems are satisfactory catalyst systems for the production of both mono- and polycyclic aromatic compounds, some authors [55–57] have studied the conversion of oxygenates in the presence of zeolites with one-dimensional porous systems of 10-membered channels in order to obtain products rich in C_{5+} HCs. Such zeolites include H-ZSM-22 (channel size, 4.6×5.7 Å), H-ZSM-23 (4.5×5.2 Å), and H-ZSM-48 (5.3×5.6 Å). It has been found that these zeolites exhibit quite high activity (methanol conversion, 90–98%) and high selectivity toward liquid HCs. All samples except for H-ZSM-48 produced a product that was rich in C_{5+} HCs and contained hardly any aromatic compounds. Judging from the large size of its channels, H-ZSM-48 offers more space for shape selectivity in the formation of aromatic HCs (see Table 1).

Lacarriere et al. [58] studied the conversion of MeOH into HCs (temperature, 450°C ; weight hour space velocity (WHSV), 2 h^{-1}) in the presence of H-MCM-22 and H-MCM-36 zeolites with MWW topology (which includes two interconnected pore systems of two-dimensional channels composed of 10- and 12-membered rings). It was found that H-MCM-22 catalyst exhibits more liquid HC selectivity (25%) than H-MCM-36 (12%). On the other hand, gasoline produced in the presence of H-MCM-36 contains mostly aliphatic HCs (85%), and the catalyst is highly resistant to coking.

An attempt to synthesize HCs from methanol in the presence of finely porous zeolites of the Erionite (ERI), Chabazite (CHA), and ZK-5 types with channel sizes of 3.6×5.1 , 3.8×3.8 , and 3.9×3.9 Å, respectively, was made in [59]; the zeolites exhibited extremely low selectivity toward liquid HCs (no more than 7.5%). The main reaction products were ethylene, propylene, and propane. The presence of appreciable amounts of methane in the composition of light HCs indirectly indicates there was active coking. With zeolites of the A, X, ZSM-4, and T types [60, 61], and molecular sieves of the aluminophosphate (AlPO-5, CoAPO-5, BeAPO-5, MgAPO-5, MnAPO-5) and silica–alumina phosphate types (SAPO), MeOH conversion is characterized by a rapid loss of catalyst activity, due to coking [62–65].

Table 1. Structural characteristics of unmodified zeolites (in H⁺ form) and their catalytic properties in the conversion of DME and MeOH

| Zeolite | ZSM-5 | ZSM-11 | MOR | Dealuminated MOR | HY | USY | ZSM-22 | ZSM-23 | ZSM-48 | ZSM-57 | FER | Beta |
|---|---|--|---|---|--|--|-----------------|-----------------|-----------------|-----------------|-----------------|----------------------------------|
| Topology | MFI | MEL | MOR | MOR | FAU | FAU | TON | MTT | MRE | MFS | FER | BEA |
| System of channels | Three dimensional | Two dimensional | One dimensional | One dimensional | Three dimensional | Three dimensional | One dimensional | One dimensional | One dimensional | Two dimensional | Two dimensional | Three dimensional |
| Twelve-membered rings | None | None | 6.7 × 7.0 Å | 6.7 × 7.0 Å | 7.4 × 7.7 Å | 7.4 × 7.7 Å | None | None | None | None | None | 7.1 × 7.6 Å 5.5 × 5.6 Å |
| Ten-membered rings | 5.1 × 5.5 Å 5.3 × 5.6 Å | 5.3 × 5.5 Å | None | None | None | None | 4.6 × 5.7 Å | 4.5 × 5.2 Å | 5.3 × 5.6 Å | 5.1 × 5.4 Å | 4.2 × 5.4 Å | None |
| Eight-membered rings | None | None | 2.9 × 5.7 Å | 2.9 × 5.7 Å | None | None | None | None | None | 3.3 × 4.8 Å | 3.5 × 4.8 Å | None |
| Channel intersection | Yes | Yes | Yes | Yes | Yes | Yes | None | None | None | Yes | Yes | Yes |
| SiO ₂ /Al ₂ O ₃ | 30 | 65 | 15 | 47 | 4.8 | 30 | 60 | 66 | 104 | 60 | 22 | 24 |
| Feedstock | MeOH | MeOH | MeOH | DME | MeOH | | | | | | | |
| T, °C | 371 | 370 | 350 | 367 | 370 | 400 | 400 | 400 | 400 | 400 | 400 | 400 |
| P, MPa | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| WHSV*, h ⁻¹ | 1.0 | 1.44 | 2.62 | 2.9 | 1.0 | 1.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 0.8 |
| Conversion, % | 99.9 | 99.0 | 62.3 | 99.6 | 54.6 | 75.3 | 90.0 | 98.0 | 95.0 | 99.0 | 99.0 | 83.0 |
| C ₅₊ HC selectivity (with respect to total HCs), % | 55.8 | 41.0 | 21.6 | 59.4 | 21.9 | 46.8 | 62.0 | 59.0 | 55.0 | 46.0 | 60.0 | 40.0 |
| Composition of liquid phase product, wt % | | | | | | | | | | | | |
| C ₅₊ aliphatic HCs | 27 | 30.0 | 36.4 | 38.3 | 84.6 | 60.7 | 98.0 | 98.0 | 80.0 | 80.0 | 98.0 | 45.2 |
| Basic compounds | C ₇ -methyl and C ₆ -dimethyl | — | C ₄ -dimethyl, C ₅ -methyl, C ₇ -methyl, C ₅ -trimethyl | n-C ₆ , C ₄ -dimethyl, C ₅ -methyl | C ₅ -methyl, C ₆ -methyl | C ₄ -methyl, C ₄ -dimethyl, C ₅ -methyl | Isoparaffins | | | — | — | Iso-C ₅ |
| C ₆₊ aromatic HCs | 73 | 70.0 | 63.6 | 61.7 | 15.0 | 39.3 | 2.0 | 2.0 | 20.0 | 20.0 | 2.0 | 54.8 |
| Basic compounds | C ₈ -C ₁₀ (xylenes) | C ₉ -C ₁₀ , durene >10 | C ₁₀₊ | | C ₉ -C ₁₁ | | | — | — | — | — | C ₁₁ -C ₁₂ |
| Stability | High | Moderate | Low | Moderate | Moderate | Moderate | Low | Low | Low | Moderate | Low | Low |
| Reference | 7 | 14 | 44 | 45 | 44 | 48 | 57 | 57 | 57 | 55 | 55 | 52 |

*WHSV is the weight hourly space velocity of feedstocks.

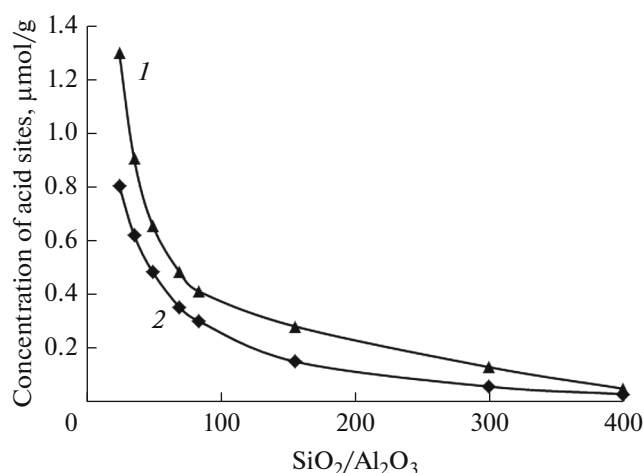


Fig. 1. Effect of the SiO₂ : Al₂O₃ molar ratio in HZSM-5 zeolite on its acid properties: (1) total number of acid sites and (2) number of strong acid sites (according to [77, 81]).

The main products are methane and small amounts of lower olefins and paraffins.

The above data suggest that the structural features of zeolites play a substantial role in the conversion of MeOH and DME into gasoline fraction HCs or respective *n*- and isoolefins with the prospect of further hydrogenation. Zeolite ZSM-5, the structural features of which provide enough volume for the conversion of DME and MeOH into liquid HCs, is the best type of zeolite for MTG.

EFFECT OF THE ACIDIC PROPERTIES OF ZEOLITES ON THEIR CATALYTIC CHARACTERISTICS

The main factor affecting the activity and selectivity of zeolites is their acidic properties. Both Brønsted and Lewis acid sites (BASes and LASes) are present in

zeolites. Brønsted acid sites are protons located near the aluminum–oxygen tetrahedra of the zeolite framework and compensate for their negative charge. Lewis acid sites are electron-accepting sites. In zeolites, these sites are either exchange cations or various aluminum-containing structures that form defects, which are referred to as true LASes.

Most researchers believe that the catalytic activity of zeolites in hydrogen form is better attributed to BASes, which differ in strength.

The catalyst selectivity for products of oxygenate conversion can be controlled by changing the ratio of these sites in the zeolite framework and their strength; these parameters in turn depend on the framework's composition (SiO₂ : Al₂O₃ molar ratio), the chemical nature of the modifier, and the means of postsynthesis treatment [66].

Effect of the SiO₂ : Al₂O₃ Molar Ratio on the Acidic Properties of Zeolites

A reduction in the content of Al atoms in the zeolite framework lowers the total number of acid sites [44, 66–80] and the fraction of strong BASes responsible for the dehydrocyclization of C₆-olefins into aromatic HCs and alkylation reactions (Fig. 1) [44, 77, 81]. This factor in turn increases the activity and selectivity of the zeolite catalyst. Upon raising the SiO₂ : Al₂O₃ ratio from 25 to 300, the zeolite's activity and selectivity toward aliphatic HCs thus increases, and the aromatic content in the resulting liquid product falls (Table 2, Fig. 2).

Along with their content, the distribution of aluminum atoms in the zeolite framework affects the ratio of different types of acid sites. It is believed that when SiO₂ : Al₂O₃ > 140, the acid sites of zeolites are homogeneous and take the form of bridging OH groups insulated from one another and bound to the aluminum atoms of the zeolite framework. When SiO₂ : Al₂O₃ < 140, the

Table 2. Conversion of MeOH and DME in to HCs in the presence of zeolites HZSM-5 with different SiO₂ : Al₂O₃ ratios (conditions: 367°C; 0.1 MPa; WHSV_{MeOH} = 1 h⁻¹)

| Parameter | SiO ₂ : Al ₂ O ₃ ratio | | | | | | | | | |
|---|---|------|-----|-----|------|------|------|------|------|------|
| | 25 | 35 | 38 | 50 | 68 | 100 | 140 | 220 | 300 | 1300 |
| Feedstock | DME | MeOH | DME | DME | MeOH | MeOH | MeOH | MeOH | MeOH | MeOH |
| Conversion, % | ≥99 | ≥99 | 99 | ≥99 | ≥99 | ≥99 | ≥99 | 97 | 97 | 2.2 |
| Selectivity toward C ₅₊ HCs (with respect to total HCs), % | 57 | 52 | 58 | 55 | 59 | 62 | 66 | 63 | 67 | 13 |
| Composition of liquid C ₅₊ HCs, wt % | | | | | | | | | | |
| Aliphatic HCs | 28 | 21 | 34 | 41 | 31 | 33 | 46 | 47 | 71 | 100 |
| Aromatic HCs | 72 | 79 | 66 | 59 | 69 | 67 | 54 | 53 | 29 | 0 |
| Reference | 73 | 71 | 73 | 73 | 71 | 71 | 71 | 71 | 71 | 71 |

acid sites are bridging OH groups that are close to one another [66, 67]. Some authors conclude that zeolite ZSM-5 with $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratios of 30–300 can be used effectively in producing gasoline from MeOH and DME [71, 72, 77, 80].

Effect of the Nature of Exchange Cations

The acidic properties of zeolites depend largely on the nature of exchange cations. Zeolites in sodium form exhibit substantially lower catalytic activity, and in some cases are completely inactive. Substituting protons for sodium cations [82] increases the overall activity of the zeolites and their selectivity toward HCs, particularly ones that are aromatic. According to the authors of [82, 83], a catalyst from which at least 50% of its sodium is removed is best for the production of gasoline from MeOH.

Table 3 shows data on the effect of exchange cations on the acidic and catalytic properties of zeolites in DME and MeOH conversion, using the example of modified ZSM-5 zeolites.

Modifying ZSM-5 zeolites with cations of nickel [86, 87], iron [97, 109], zinc [7, 26, 90, 103, 104, 109, 126–134], gallium [84, 94, 101, 104–107], silver [87, 96], copper [85, 87, 88], palladium and other noble metals [87], and rare-earth and other elements [70, 98, 100, 102] alters the acidic properties of the zeolites, and thus their activity and selectivity toward liquid HCs.

Modifying zeolite HZSM-5 with nickel [74] and copper compounds [84, 85] increases the total number of acid sites and redistributes the acidity spectrum in favor of strong sites (type II).

Introducing nickel (see Table 3) into HZSM-5 zeolite ($\text{SiO}_2 : \text{Al}_2\text{O}_3 = 300$) thus has a substantial effect on the catalyst's activity and the group HC composition of the resulting gasoline: with complete DME conversion, the content of $\text{C}_5\text{--C}_8$ isoparaffins grows from 42.7 to 61.9 wt % with a reduction in the content of $\text{C}_8\text{--C}_{10}$ aromatic compounds, from 39.6 to 24.2 wt %. The durene content in particular falls from 7.5 to 4.0 wt % [74]. Using MeOH as the feedstock raises the content of $\text{C}_6\text{--C}_{11}$ aromatic compounds in the composition of the liquid phase products to 60% [86, 87].

When HZSM-5 ($\text{SiO}_2 : \text{Al}_2\text{O}_3 = 90$) is modified with copper (see Table 3), the conversion of MeOH rises from 89 to 99%, testifying to enhancement of the catalyst's activity. The selectivity toward liquid HCs also grows from 69 to 87%. Both findings are attributable to an increase in the total number of acid sites, due to the formation of type II sites [85, 88].

Modification with molybdenum and zinc conversely reduces the total acidity of HZSM-5 zeolite (see Table 3). The patterns of change in the activity and selectivity of the modified zeolites are in this case different. Modification with molybdenum lowers the conversion of MeOH (from 100 to 80%) and the selec-

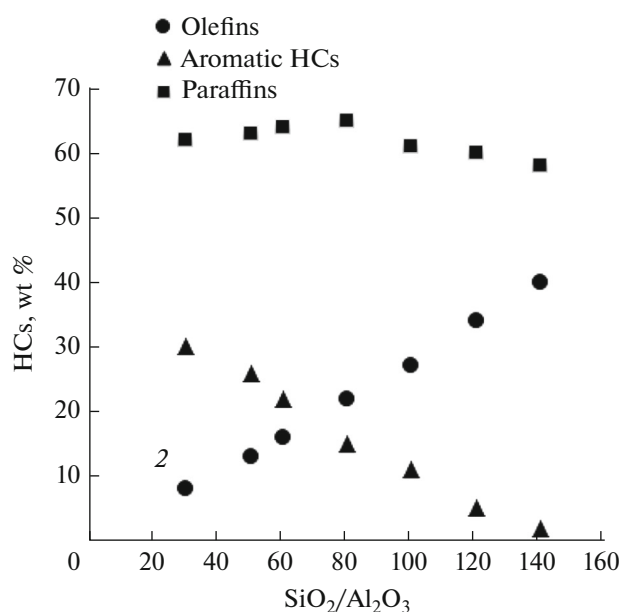


Fig. 2. Effect of the $\text{SiO}_2 : \text{Al}_2\text{O}_3$ molar ratio in HZSM-5 zeolite on the composition of gasoline produced from DME: $T = 400^\circ\text{C}$; $P = 0.1 \text{ MPa}$; and $\text{WHSV}_{\text{DME}} = 7 \text{ h}^{-1}$ (according to [80]).

tivity toward the liquid HC (from 54 to 39%). This is followed by an increase in the content of aromatic compounds ($\text{C}_6\text{--C}_8$) in the resulting gasoline (from 13.5 to 21.5 wt %) [89]. When modified with zinc, we observe an increase in selectivity toward the liquid product (from 56 to 68%), and in its aromatic content (from 35.6 to 46.9%) [89]. This finding can be attributed to modification with molybdenum leading to the suppression of strong acid sites [89]; with zinc, the concentration of weak sites is reduced and the strength of type II sites grows [4, 90, 91].

Effect of the Means of Modification on Acidic and Catalytic Properties

The way in which the modifying additive is introduced plays an important role in the change in the acidic characteristics of zeolites, and thus their activity and selectivity in the formation of liquid HCs from MeOH and DME.

The authors of [85] showed that modifying HZSM-5 zeolite ($\text{SiO}_2 : \text{Al}_2\text{O}_3 = 90$) with copper (1.9 wt % CuO) via ion exchange has a stronger effect on the total number of acid sites than the one caused by impregnation, and we observe a redistribution of the acidity spectrum in favor of strong sites (see Tables 3, 4). With impregnated samples, the total concentration of acid sites grows from 0.77 to 0.81 mmol NH_3/g upon raising the amount of introduced copper from 1.9 to 7 wt % (see Table 4).

Table 3. Effect of exchange cations on the acidic and catalytic properties of ZSM-5 zeolites in DME and MeOH conversion

| Parameter | SiO ₂ : (MeO* + Al ₂ O ₃) molar ratio | | | | | | | | | |
|--|---|----------------------|-------------------------|--------------|------------------------------|-----------------------|----------------------|---------------------------------------|------------------|------------------------------|
| | 90 | 90 | 300 | 60 | 50 | 90 | 42 | 132 | 400 | 35 |
| Modifier (Me) | CuO | CuO | Ni | Ni | Mo | ZnO | Ga | -[Ga]- | -[Fe]- | La, Zn |
| Me content, wt % | 1.9 | 7.0 | 1 | 1 | 7.5 | 1.16 | 1.9 | | | |
| Means of introducing Me | Ion exchange | Impregnation | Impregnation | Impregnation | Impregnation | Ion exchange | Ion exchange | Direct synthesis | Direct synthesis | Ion exchange, impregnation |
| Acidity of original ZSM-5, mmol/g | 0.770 | 0.770 | 0.129 | — | 0.480 | 0.563 | 0.900 | 0.600 | 0.050 | 0.757 |
| Acidity of modified ZSM-5, mmol NH ₃ /g | 0.970 | 0.810 | 0.164 | — | 0.330 | 0.554 | 0.852 | 0.480 | 0.051 | 0.641 |
| Pattern of change in acidity spectrum | Favors type II sites | Favors type II sites | Favors type II sites | — | Favors type I sites | Favors type II sites | Favors type II sites | At the expense of type I and II sites | — | Favors type II sites |
| Pattern of change in the strength of acid sites | — | — | Reduction for type II | — | Reduction for types I and II | Reduction for type II | Increase for type II | Reduction for type II | — | Reduction for types I and II |
| Feedstock | MeOH | MeOH | DME | MeOH | MeOH | MeOH | MeOH | MeOH | MeOH | DME |
| T, °C | 392 | 392 | 350 | 450 | 400 | 390 | 427 | 370 | 450 | 340 |
| P, MPa | 0.1 | 0.1 | 1.5 | 0.45 | 0.1 | 0.5 | 0.1 | 0.1 | 0.1 | 10 |
| WHSV, h ⁻¹ | 5.8 | 5.8 | 8 | 0.5 | 2.0 | 3.2 | 3.2 | 7.9 | 2.55 | 2.7 |
| Feedstock conversion, % | 100 | 99.0 | 100 | 100 | 80 | 99 | 99 | 99 | 99.5 | 99.9 |
| Liquid HC selectivity, % | 88.7 | 87.1 | 60.0 | 59.0 | 39.0 | 68.0 | 50.8 | 41 | 28.8 | 78.0 |
| Composition of liquid phase product, wt % | | | | | | | | | | |
| C ₅₊ aliphatic HCs | 67.8 | 61.9 | 75.8 (61.9–soparaffins) | 40.0 | 78.5 | 53.1 | 51.8 | 91.5 | — | 89.5 (75–isoparaffins) |
| C ₆₊ aromatic HCs | 32.2 | 28.1 | 24.2 | 60.0 | 21.5 | 46.9 | 48.2 | 8.5 | — | 10.5 |
| Reference | 85 | 85 | 74 | 87 | 89 | 90 | 101 | 104 | 109 | 17.103 |

*For samples prepared by directly introducing cations of active elements during zeolite synthesis.

Table 4. Characteristics of the acidity and catalytic properties of Cu–HZSM-5 samples in the conversion of MeOH into HCs ($T = 392^{\circ}\text{C}$; $P = 0.1\text{ MPa}$; $W_{\text{MeOH}} = 5.8\text{ h}^{-1}$) according to [85]

| [CuO], wt % | Means of treatment | Acidity, mmol NH_3/g | MeOH conversion, % | C_{5+} HC selectivity, wt % | Content of aromatic HCs in the product, wt % |
|-------------|--------------------|--------------------------------------|--------------------|--------------------------------------|--|
| 0 | — | 0.77 | 88.7 | 68.7 | 18.4 |
| 1.9 | Ion exchange | 0.97 | 100 | 88.7 | 32.2 |
| 1.9 | Impregnation | 0.76 | 96.4 | 86.4 | 24.6 |
| 7.0 | Impregnation | 0.81 | 99.0 | 87.1 | 28.1 |

Table 5. Acidity and catalytic properties of Zn–HZSM-5 in the conversion of MeOH to HCs ($T = 390^{\circ}\text{C}$; $P = 0.5\text{ MPa}$; $W_{\text{MeOH}} = 3.2\text{ h}^{-1}$; length of reaction, 40 h) according to [90]

| [Zn], wt % | Means of treatment | Acidity | | | MeOH conversion, % | C_{5+} HC selectivity, wt % | Content of aromatic HCs in product, wt % | Stable on-stream time, h |
|------------|--------------------|------------------------------------|-----------------|---------|--------------------|--------------------------------------|--|--------------------------|
| | | total, mmol NH_3/g | type II/ type I | LAS/BAS | | | | |
| 0 | — | 0.563 | 3.27 | 0.27 | 99 | 56.1 | 35.6 | 70 |
| 1.16 | Ion exchange | 0.554 | 3.22 | 2.51 | 99 | 68.0 | 46.9 | 60 |
| 0.98 | Direct synthesis | 0.553 | 3.3 | 1.08 | 99 | 63.2 | 43.0 | 130 |
| 1.13 | Impregnation | 0.554 | 3.1 | 1.47 | 92 | 63.7 | 43.1 | 40 |
| 1.02 | Mechanical mixing | 0.512 | 3.1 | 0.55 | 99 | 57.9 | 38.1 | 60 |

Tests of samples for MeOH conversion showed that the means of modification affects the catalytic characteristics of the zeolite uniformly: the conversion of MeOH, the yield of liquid HC, and the content of aromatic HC in the liquid product for the sample prepared via ion exchange are higher than the respective parameters for the impregnated samples (see Table 4).

In the last 20 years, researchers have shown considerable interest in zinc- [69, 92, 93] and gallium-containing ZSM-5 zeolites [94], since these materials are highly active in different hydrogen transfer-based reactions (e.g., the hydrogenation of unsaturated HCs, the hydrocracking of alkanes, and the aromatization of light alkanes). Zinc and gallium ion-exchange forms of ZSM-5 zeolite also allow us to synthesize gasoline fraction HCs from MeOH [4, 21, 86, 95–97] and DME [73, 98–100] selectively.

The authors of [90] studied the effect of the way in which zinc cations (no more than 1.16 wt % ZnO) are introduced into the composition of HZSM-5 ($\text{SiO}_2 : \text{Al}_2\text{O}_3 = 90$) on the acidic properties of the zeolite. The following means of introduction were compared: impregnation, ion exchange, the mechanical mixing of ZnO and HZSM-5, and introduction during the synthesis of ZSM-5 zeolite. It was shown that during conventional ion exchange, the acidic properties of the zeolite are considerably altered: the total number of acid sites of the zeolite falls, due to a reduction in the number of weak acid sites (Table 5). An increase in the

fraction of strong acid sites in the 1.16%Zn–ZSM-5 sample prepared via ion exchange raises the process's selectivity toward the liquid product (from 56.1 to 68.0%) and the content of aromatic compounds in the product (from 35.6 to 46.9%) [90].

Using X-ray photoelectron spectroscopy and extended X-ray absorption-edge fine-structure spectroscopy, the authors of [90] showed that the state and distribution of active sites in Zn–HZSM-5 samples prepared by different means differ greatly:

- In a sample prepared via the physical mixing of ZnO and HZSM-5, zinc was present mostly in the form of ZnO macroparticles on the zeolite's surface.
- A sample prepared via impregnation contained a number of ZnO nanoclusters dispersed in the zeolite channels and ZnOH^+ Lewis sites that formed during the interaction between zinc cations and BASes.
- ZnOH^+ Lewis sites predominated in samples prepared by introducing zinc via ion exchange and during zeolite synthesis.

A reduction in Brønsted acidity, due to the interaction between zinc cations and these sites to form ZnOH^+ Lewis sites, inhibited the reaction of hydrogen transfer and suppressed the formation of alkanes. There was a linear correlation between the number of surface ZnOH^+ sites and the catalytic properties of Zn–HZSM-5: the sample prepared via ion exchange was characterized by a high concentration of ZnOH^+

sites and the greatest selectivity toward liquid HCs and aromatic compounds.

Similar results were obtained in [4, 17, 21, 69, 86, 101], where HZSM-5 zeolites ($\text{SiO}_2 : \text{Al}_2\text{O}_3 = 36\text{--}42$) were modified with zinc cations. The cited authors attributed the high content of aromatic (67%) and unsaturated compounds (13%) in the liquid product of MeOH conversion to the replacing of hydrogen cations with zinc cations lowering the zeolite's acidity from 0.900 to 0.782 mmol NH_3/g , due to a reduction in the number of sites of both types. This slowed the rate of hydrogen transfer between the carbenium ions and the alkenes and thus reduced the alkane yield. The remaining strength of these sites provided a fairly high yield of the liquid product (71.7%).

Treating $\text{NH}_4\text{--ZSM-5}$ zeolite ($\text{SiO}_2 : \text{Al}_2\text{O}_3 = 35$) with an aqueous solution of lanthanum nitrate under different ion exchange conditions (in air at a temperature of 90°C , and in an autoclave at high temperatures of $185\text{--}220^\circ\text{C}$) lowers in the total number of acid sites from 0.757 to 0.225 mmol NH_3/g [102]. The observed drop in the fraction of strong acid sites in the acidity spectrum in favor of medium-strength sites reduces the aromatic content (from 10.5 to 5.5 wt %) and raises the isoparaffin HC content (from 69 to 76 wt %) in the resulting liquid product with a selectivity of 83% in DME conversion. A similar effect on the acidic and catalytic properties of the catalyst is observed after pretreating $\text{NH}_4\text{--ZSM-5}$ ($\text{SiO}_2 : \text{Al}_2\text{O}_3 = 35$) with an aqueous solution of zirconyl nitrate [103].

The presence of palladium (no more than 0.5 wt % PdO) in catalysts ensures a fairly high rate of intermolecular hydrogen transfer, which lowers the concentration of durene in the composition of the resulting gasoline to 0.2 wt %.

Introducing gallium cations (1.9 wt % Ga) into HZSM-5 zeolite ($\text{SiO}_2 : \text{Al}_2\text{O}_3 = 37\text{--}42$) via ion exchange [21, 86, 101] (see Table 3) affects the acidic and catalytic properties of the zeolite in a manner similar to modification with zinc. We observe a drop in the total acidity of the zeolite at the expense of weak sites, and an increase in the strength of type II acid sites. This raises the selectivity toward gasoline (from 44.0 to 50.8%) and its aromatic content (from 40.3 to 48.2 wt %) [101].

The isomorphous incorporation of trivalent gallium into the structure of ZSM-5 zeolite ($\text{Si} : \text{Ga} = 66$) during its synthesis [104] results in the formation of a catalyst that is insufficiently active for the conversion of primary products formed from MeOH. The concentration of aromatic compounds in the resulting gasoline is in this case as low as 8.5% (xylenes and trimethylbenzene), which is fairly low for an element that is known as one of the best modifiers in the aromatization of lower alkanes and alkenes [84, 94, 105–107]. The authors of [104] attributed this to changes in the acidic properties of the zeolite that occur during modification, i.e., a drop in the concentration of sites

of both types (see Table 3) and a simultaneous reduction in the strength of type II sites. Analyzing the catalytic properties of samples of isomorphously substituted H--[Ga]--ZSM-5 with different concentrations of gallium, the authors of [108] concluded that when $\text{Si} : \text{Ga} = 66$, the concentration of gallium in the zeolite's framework is relatively low and the generated BASes (Si--OH--Ga) form DME from MeOH. Higher gallium concentrations ($\text{Si} : \text{Ga} = 17.5$) ensure the formation of additional active extra-framework gallium sites with Lewis acidity. These enhance the strength of the Si--OH--Ga sites and thereby increase the aromatization activity of the catalyst and lower the yield of olefins.

Introducing iron into the zeolite's structure during its synthesis conversely increases the total number of acid sites in H--[Fe]--ZSM-5 zeolite (molar ratio of $\text{SiO}_2 : (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) = 100\text{--}400$, $\text{Al} : \text{Fe} = 1$) with the generation of strong BASes (Al--(OH)--Si) and new Fe--(OH)--Si sites, thereby ensuring high activity of at least 99.5% in methanol conversion [109]. The aromatic HC content in the produced high-octane gasoline is in this case as high as 72% (xylenes) [97].

The direct introduction of cations of active elements during synthesis ensures a uniform fine distribution of active sites throughout the zeolite's volume, thereby eliminating the possibility of metal particle agglomeration and the resulting loss of a substantial portion of active sites. The high stability of the resulting active sites can be attributed to their being tightly bound to the zeolite framework. The introduction of metal cations into the zeolite framework can be accompanied by neutralization of a portion of the proton sites (BASes) and the formation of new LASes, so the range of surface groups responsible for reactions leading to the formation of target products from MeOH and DME can be expanded [110–116]. Isomorphously substituted zeolites are typically more active than zeolites modified via ion exchange or impregnation.

However, some studies do not confirm the above. The direct incorporation of boron into the structure of ZSM-5 ($\text{SiO}_2 : \text{Al}_2\text{O}_3 = 50$) produces samples that are actually less active in MeOH conversion ($T = 370^\circ\text{C}$; $P = 0.1$ MPa; $W_{\text{DME}} = 1$ h $^{-1}$) than the unmodified zeolite: conversion falls from 36 to 21%. Due to the redistribution of hydrogen, the HC composition of the products in this case contains hardly any aromatic compounds, while the content of unsaturated $\text{C}_3\text{--C}_5$ HCs falls from 66 to 57% in favor of $\text{C}_4\text{--C}_6$ aliphatic compounds (an increase of 22 to 32%) [117]. Courdurier and Chu [117–119] attribute these results to the suppression of strong BASes by the boron, which is incorporated into the zeolite structure to form a weaker B--(OH)--Si site and reduces the total acidity of the zeolite. A similar effect on acidic properties is observed upon treating pentasil with an H_3BO_3 solution [118, 120]. The low melting point of B_2O_3 oxide

means it readily reacts with the zeolite matrix during calcining, and the reaction leads to the partial replacement of the framework Si and Al atoms with boron and the formation of weaker B—(OH)—Si sites. Some of the boron forms a borosilicate compound on the zeolite surface, thereby imposing additional limitations on diffusion.

The above data on the effect of exchange cations on the acidic and catalytic properties of zeolites in DME and MeOH conversion suggest that the highest selectivity for gasoline fraction HCs is exhibited by zeolites ZSM-5 that contain copper, zinc, nickel, gallium, lanthanum, and zirconium cations introduced via ion exchange or direct incorporation into the zeolite structure. Compared to impregnation, these means ensure a more uniform distribution of active sites throughout the zeolite's volume.

Effect of Postsynthesis Treatment

The currently available ways of changing the acidic properties of zeolites and increasing their catalytic activity in converting methanol into HCs include acidic, alkaline, and steam heat treatment. The last of these is commonly used in the production of commercial catalysts [121]. Acidic (using oxalic, hydrochloric, or hydrofluoric acids) [122, 123] and steam heat treatment [124, 125] cause dealumination and thereby affect (to varying degrees) the crystallinity of the zeolite.

According to [106], the selective removal of aluminum from the framework of zeolite H—Ga—ZSM-5 (Si : (Ga + Al) = 33) during steam heat treatment ($T = 600^\circ\text{C}$; H_2O , 48 mol %) increases the Si : Al ratio. The number of strong acid sites in this case grows from 0.21 to 0.25 mmol/g, ensuring 15 to 18 wt % more selectivity for gasoline produced via methanol conversion ($T = 400^\circ\text{C}$; $P = 0.1$ MPa; $W_{\text{MeOH}} = 0.22$ h⁻¹) and a 30 to 35 wt % increase in its content of C₆–C₈ aromatic compounds.

Selective dealumination also occurs upon treating modified 0.5ZnO–7CuO–HZSM-5 zeolite (SiO₂ : Al₂O₃ = 90) with oxalic acid, and the removal of active sites on the outer surface is observed [123]. This treatment lowers the concentration of both strong and weak acid sites. As a consequence, the formation of heavier products (which require more space) on the outer surface and in the near-surface layer of the zeolite is excluded. This ensures easier access of MeON to the active sites located in the zeolite pores and increases the efficiency of the catalyst.

Acidic treatment of HZSM-5 zeolite (SiO₂ : Al₂O₃ = 50) with an HF solution (concentration, 0.5–2 M) led to the removal of framework Si and Al, since HF reacts with both silicon and aluminum, as was shown in [126, 127]. It was found that dealumination is more pronounced than desilication. After treating the zeolite with hydrofluoric acid, the total number of acid sites of the zeolite fell by half, due mostly to a drop in the

number of weak sites. These changes in acidic properties were attributed to a reduction in the liquid HC selectivity (from 30.2 to 25.3 wt %), due to a drop in the yield of C₇–C₉ methyl-substituted benzenes (from 18.6 to 13.8%) during MTG ($T = 400^\circ\text{C}$; $P = 1$ atm; $W_{\text{MeON}} = 10$ h⁻¹).

Alkaline treatment of HZSM-5 zeolite (SiO₂ : Al₂O₃ = 30) with a NaOH solution (0.20 M) resulted in desilication with an almost 150% drop in the SiO₂ : Al₂O₃ molar ratio [128–130]. The total number of acid sites in the zeolite in this case fell from 0.859 to 0.533 mmol/g at the expense of sites of both types (I and II). The remaining strength of these sites in the leached zeolite produced an almost 500% increase in the content of C₇ isoparaffins in the composition of the resulting gasoline [129] and a 49 to 56% increase in liquid HC selectivity in methanol conversion ($T = 400^\circ\text{C}$; $P = 1$ atm; $W_{\text{MeOH}} = 8$ h⁻¹).

To produce gasoline with low contents of benzene (no more than 0.1 wt %) and durene (no more than 2.7 wt %) from DME ($T = 350^\circ\text{C}$; $P = 0.1$ –1.4 MPa; $W_{\text{DME}} = 9.9$ h⁻¹), HZSM-5 zeolite (SiO₂ : Al₂O₃ = 50) was treated with a phosphoric acid solution in [22, 131]. This treatment greatly reduced the number of strong BASes (by 80%) without affecting the SiO₂ : Al₂O₃ molar ratio in the zeolite [131]. This effect was attributed to phosphoric acid being capable of hydrolyzing alumina weakly bound to the zeolite framework and removing it from the structure to form inert aluminum phosphate (according to ²⁹Si, ²⁷Al, and ³¹P magic angle–spinning nuclear magnetic resonance spectra and Al K-edge X-ray absorption near-edge structure spectra) [131].

In recent years, zeolites have been subjected to innovative postsynthesis treatments with, e.g., ultrasound and microwaves [132]. A uniform fine distribution of the active metal throughout the entire zeolite volume can be ensured via ultrasonic treatment upon introducing a modifying additive into the zeolite. Studies of the effect of ultrasound on the physicochemical properties of 5ZnO–7CuO–HZSM-5 (SiO₂ : Al₂O₃ = 130) [133] show that compared to samples prepared via impregnation, acoustic cavitation during ultrasonic treatment increases the degree of dispersion of CuO and ZnO particles (11.3 and 9.6 nm, respectively) without changing the zeolite structure. As a consequence, more accessible active sites on the zeolite surface raise the total number of acid sites and therefore increase the catalyst's activity through greater adsorption of methanol. Gasoline produced with a selectivity of 96% is up to 74% aromatic HCs (mostly xylenes).

The above data suggest that the postsynthesis treatment of zeolites ensure not only a change in their total acidity, but also optimization of the number of acid sites, their strength distribution, and their ratio. This

allows us to control the selectivity and stability of the catalysts in converting methanol and DME into HCs.

CONCLUSIONS

The main parameters responsible for the selectivity of catalysts in MTG reactions are now fairly obvious. The data described in this review suggest that shape selectivity is a fundamental characteristic of highly stable zeolite catalyst for the conversion of oxygenates into liquid HCs. The regions of channel intersection in HZSM-5 zeolite provide enough volume for ring-forming reactions and intermolecular hydrogen transfer, during which a mixture of alkenes can be converted to alkanes and aromatic compounds that can freely leave the zeolite channels.

Catalyst selectivity toward products of oxygenate conversion can be controlled by changing the acidic properties of the zeolite, which in turn depend on the composition of the framework and the chemical nature of the modifier.

It was shown that ZSM-5 zeolite with a SiO₂ : Al₂O₃ ratio of 30–300 is effective for producing gasoline from oxygenates. The presented data on the effect of exchange cations on the acidic and catalytic properties of ZSM-5 zeolites in the conversion of DME and MeOH to HCs show that the highest selectivity toward gasoline fraction HCs is exhibited by zeolites that containing copper, zinc, nickel, gallium, lanthanum, and zirconium cations. One way of controlling catalyst selectivity in converting oxygenates into HCs is post-synthesis modification of zeolites, aimed at optimizing their acidic properties.

In addition to the factors described above that affect the catalyst selectivity in MTG, ZSM-5 zeolite has textural and morphological characteristics that determine the mass transfer in catalytic processes. High hydraulic resistance and limitations on diffusion in reactions, which play a major role in the industrial use of zeolites, can be circumvented by using structured mesoporous materials and nanocrystalline zeolites, a discussion of which is beyond the scope of this review.

In coming years, after the commercialization of several MTG processes, interest in this field of research will most probably grow, particularly when it comes to the manufacturing of such high-added value products as environmentally friendly high-octane motor fuels enriched with trimethyl-substituted C₇–C₈ paraffins.

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